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SOME ASPECTS OF THE ELECTRONIC THEORY APPLIED TO ORGANIC CHEMISTRY.

by

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Part I

THE REDUCTION OF THE NITRO GROUP AS A FUNCTION OF ITS POLARITY.

According to the polar valence theory of Fry and others(1), an element or group may have a positive or negative polarity, depending on various conditions. Even the electron displacement theory of Lewis and Lucas(2) allows of varying degrees of polarity due to the position of the displaced electron pair. Halogen is usually considered to be electronegative. Many instances, however, of positive halogen(3) have been given. Noyes and others(4) have shown that positive halogen exerts twice the oxidizing power of elementary halogen. Nicolet(5) has used this property as a test for positive halogen in aromatic compounds with marked success. Halogen of positive polarity is removed with stannous chloride while negative halogen is not. Reduction of halogen is therefore a function of its polarity. Nicolet found that halogen, in benzene compounds, when ortho or para to a strongly negative group, assumed a positive polarity.(6)

Evidence that nitro groups may vary in polarity also, depending on their position relative to other groups, has been obtained in this laboratory by Clark and Carter(7), by their work on the replaceability of nitro groups from the nucleus of various aromatic compounds on heating with sodium hydrate or sodium ethylate solutions. A nitro group, when ortho or para to a strongly positive group assumes a negative polarity, or vice versa. Since positive halogen has exceptional oxidizing power, it might be reasonable to expect that nitro groups of different polarity would likewise require different amounts of reducing agent for complete reduction, as shown by the following equations.

(a) In terms of the electronic theory.

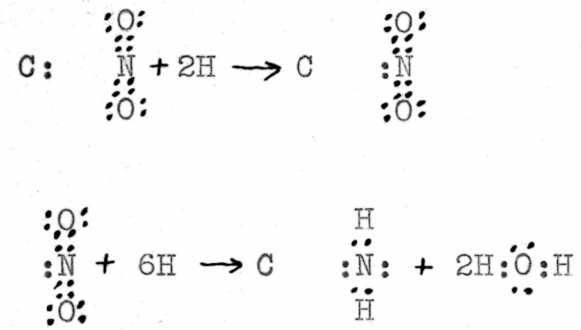
$$\overset{+}{N}O_2 + \overset{\ominus}{H} = (NO_2)$$

$$(NO_2) + \overset{\ominus}{H} = \overset{-}{N}O_2$$

$$\overset{-}{N}O_2 + 6H = NH_2 + 2H_2O$$

i.e. to reduce nitrogen from a positive valence of 5 to a negative valence of 3 requires 8H, whereas to reduce it from a positive valence of 3 to a negative valence of 3 requires only 6H.

(b) In terms of the displacement theory.



Thus for maximum differences in polarity, three-fourths of the reducing agent required to reduce a positive nitro group would be sufficient for one that was negative.

The complete reduction of the nitro group by means of titanous sulphate(8) and other reducing agents(9) provides a standard method for its quantitative determination. According to the above theory different amounts of reducing agent should be used for the reduction of equivalents of positive and negative nitro substituents. If such is the case the above method of reduction would serve as a ready means of differentiating between nitro groups of different polarity. As far as can be ascertained from the literature the method has not been applied to compounds containing nitro groups of different polarity. Accordingly the following measurements have been made.

The analytical procedure was based on the method of Callan and Henderson(8) and may be thus outlined. A 5% solution of titanous sulphate in dilute sulphuric acid was prepared and stored under hydrogen. A solution of ferric alum was standardized in terms of the titanous sulphate solution. The titanous sulphate solution was standardized as follows: A weighed amount, about 0.1 gram, of carefully recrystallized p-nitroaniline was dissolved in alcohol and dilute sulphuric acid; an excess of titanous sulphate was added, the mixture was boiled for five minutes in an atmosphere of carbon dioxide, cooled, and the excess titanous sulphate titrated with the ferric alum, using potassium thiocyanate as the indicator. Thus the amount of nitro group equivalent to one cc. of the standard titanous sulphate solution was determined. The following compounds were then analysed for nitro groups by the same procedure, the results being tabulated below.

Compound	% Nitro G. by analysis	% Nitro Group calculated.
o-dinitrobenzene	54.70	54.76
m-dinitrobenzene	54.65	54.76
p-dinitrobenzene	54.66	54,76
o-nitrobenzenesulphonic acid	22.61	22.66
m-nitrobenzenesulphonic acid	22.64	22.66
p-nitrobenzenesulphonic acid	22.60	22.66

table continued:

o-nitrophenol	33.05	33.10
m-nitrophenol	33.09	33.10
p-nitrophenol	33.13	33.10
o-nitrochlorbenzene	29.20	29.21
m-nitrochlorbenzene	29.24	29.21
p-nitrochlorbenzene	29.16	29.21

The compounds tabulated, from consideration of the theories outlined, should contain nitro groups of different polarity. For example. ortho and para dinitrobenzene should contain one positive and one negative nitro group, while the nitro groups in meta-dinitrobenzene should have the same polarity, probably both positive, judging from their slight reaction with sodium hydrate(7). Nicolet, however, has shown that a halogen is not influenced by a substituent in the meta position; thus a halogen when meta to a strongly electropositive group is, contrary to expectation, not electropositive. The nitro groups in ortho and para nitrophenol are undoubtedly electropositive. The compounds which we would expect to show irregularities in analysis are ortho and para dinitrobenzene and ortho and para nitrobenzenesulphonic acid. They give,however. perfect analyses like the others.

The quantitative method of analysis for nitro groups has been found to apply for the determination of all nitro groups regardless of polarity.

The fact that the method holds for such compounds as ortho and para-dinitrobenzene, proves conclusively that the reduction of positive and negative nitro groups to amino groups shows no parallelism to the behaviour of the positive and negative halogens with stannous chloride.

I wish to thank Dr. Clark for advice and aid during this study.

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PART II

CATHODIC HALOGEN

ELECTROLYSIS OF THE HALOGENYL AMIDES.

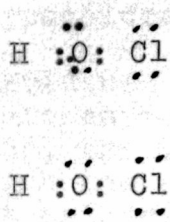
As indicated in the preceding paper,much evidence has been accumulated for the existence of the so-called "positive" halogen. The halogenyl compounds, where the halogen replaces the hydrogen in the amino group, constitute one type of compound where the halogen is thought to be positive. The halogenyl amides were studied by Selivanow(1). Houben gives a summary of their properties, which correspond closely to those of other compounds containing halogen of positive polarity. Nicolet's test(2) indicates also that the halogen is positive. It is the aim of this work to furnish further definite proof by electrolyzing a representative number of these compounds.

In a previous paper(3) from this laboratory, a review of the few cases of the separation of halogen as a cation has been presented. The authors obtained cathodic iodine on the electrolysis of cyanogen iodide in a pyridine solution between silver electrodes. Other cases of bromine and iodine migrating to the cathode on electrolysis were also found in this laboratory;(4) the bromine of bromyl succinimide went entirely to the cathode, while the iodine and bromine of iodyl succinimide and bromyl acetamide went largely to the cathode,acetonitrile being used as the solvent. These results are analogous to those obtained by Moer(5) and later by Bardwell(6), who prepared anodic hydrogen by the electrolysis of various molten hydrides.

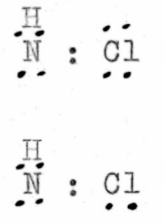
The existence of positive halogen compounds should be explained by the advocates of the two major theories of valence(7),--the electron bond theory of G.N.Lewis, Langmuir, and others and the electronic theory of J.J.Thomson,Stieglitz,Fry and others. The electrolysis of halogenyl amides furnishes additional data to be considered, particularly in regard to the existence of electromers.

According to the electron bond theory, the polarity of the bond depends upon the position of the bonding pair of electrons,held jointly in the shells of the two atoms. Thus a negative element or radical draws toward itself the electron pair,whereas an electropositive group pepels or attracts these electrons to a less extent. In a non-polar union, the bonding pair must lie midway between the two atomic centers. In a polar union one element may assume full possession of the bonding pair, and we have complete ionization. If according to Lewis the union between oxygen and chlorine in hypochlorous acid is non-polar, we will have formula(1) for hypochlorous acid and the corresponding formula (2) for a chloryl amide.

see page 6.



(1) and



(2)

(3) and

(4)

In terms of his hypothesis only positive ions as hydrogen lithium, glucinum, and carbon of the positive ion of triphenyl methyl have less than eight electrons in the outer shell. However, Noyes and Wilson(8) confirmied Pelouze's(9) work that chlorine monoxide, not hypochlorous acid, escapes when air is bubbled through the latter, showing the existence of positive chlorine having only six electrons in the outer shell. Accordingly some of the hypochlorous acid must exist as indicated in formula (3), the dotted line indicating the formation of H_2O and Cl_2O from 2HOCl. If hypochlorous acid has two electromers, it is probable that the halogenyl amides also will have two electromers as indicated above, formula (4) indicating the positive nature of the chlorine atom.

Our electrolytic results indicate such isomers in solution, for example, bromyl acetamide in absolute alcohol and nitromethane deposited bromine on the anode, in acetonitrile (6) it deposited bromine on both electrodes, while in pyridine it liberated bromine entirely on the cathode.

In a recent article Kharasch and Darkis(10) pointed out the existence of two electromers of 2-Pentene, for which they gave electron displacement formulae. Other compounds containing double bonds may also exist in two forms, if the radicals attached to the carbon atoms of the double bond are very close in polarity. Ultra-violet light was found to change the proportion of the two isomers present in 2-Pentene. This is a departure from the original theory of Lewis where the bonding pair was considered to be fixed in a particular compound. The existence of such partially polar electromers would account for our experimental results.

According to the electronic theory the atoms are held to-gether by the static attraction between them, after the transfer of an electron from one atom to another, and not by a magnetic attraction as suggested by Lewis(11). The polarity of the resulting atoms is indicated by plus and minus signs which Stieglitz and Fry(12) recently pointed out were not to be interpreted as meaning ionic polarity.

According to Fry one electromer may be changed into the other, by the transference of an electron from one atom to the other, a self oxidation-reduction process within the molecule. The electronic formula assigned to a compound must explain its behavior in such processes as electrolysis, hydrolysis and oxidation-reduction. As pointed out, Noyes has found

that hypochlorous acid presents two types of ionization.

Evidence for the existence of the electromers of various halogenyl amides and imides was obtained in this investigation, the stability of each electromer apparently depending upon the solvent. Clark and Streight(3) previously showed that cathodic iodine was obtained only on electrolyzing cyanogen iodide in pyridine; in twelve other solvents only anodic iodine was found.

EXPERIMENTAL PART

All of the solvents employed were most carefully dried after being thoroughly purified. The pyridine was dried according to MacClung(13) with modifications and distilled. In order to remove all traces of water the fraction coming over at 114 to 116°C. was mixed with freshly ignited barium oxide, and shaken in an automatic shaker for two days. The solution was filtered and redistilled over additional barium oxide.The acetonitrile was redistilled three times over phosphorous pentoxide, and kept in a tightly corked bottle. Other solvents were dried in the usual manner.

Solutions 0.1 molar were used for the most part. These were electrolyzed in a V shaped cell having a stopcock of large bore at the bottom. A loose plug of carefully dried cotton wool was placed in the bore, to prevent diffusion of non-adhering precipitate.

The electrodes were made of silver , the ends of which were 3 cm. apart; before electrolysis they were coated with a thin film of silver bromide by exposure to bromine vapor, to assist the precipitate to adhere to the surface. The electrical connections were the same as in previous work(5,6).

Electrolysis was allowed to continue until sufficient precipitate of silver halide was deposited for analysis, usually from four to ten hours. After electrolysis the stopcock was turned, and the total precipitate in each compartment, if any, after being washed with acetone to remove all adhering solvent, was tested for halogen by Beilstein's (14) test. The precipitate was also tested for halogen with manganese dioxide and concentrated sulphuric acid in the usual way. In some cases quantitative analyses were made.

ELECTROLYSIS

Bromyl acetamide was prepared by Hofmann's (17) method, and was purified from absolute ether. The compound was dried over night in an oven at 50° C., and gave a product with a melting point of 104° C. A stringy precipitate formed on the cathode in pyridine which on analysis proved to be silver bromide. The percentage of bromide found was 40.73; the calcu-

lated percentage, 42.55. Some free bromine was also found in the cathode solution, which colored it red. After some time a small precipitate formed on the anode, which gave no test for halogen. In a solution of absolute ethyl alcohol and also of nitromethane, silver bromide formed solely on the anode.

Iodyl Acetamide.

This compound was prepared according to Boismenu, (16) and had a melting point of 143° C. after purifying from dry chloroform. In acetonitrile the halogen went to both electrodes. In pyridine the halogen went entirely to the cathode. This solution was originally a pale straw color, but after running for several hours the cathode liquid became reddish, while the anode compartment became colorless. A small white crystalline precipitate formed on the anode after precipitation had started on the cathode. It had no definite melting point, and gave no test for halogen.

Iodyl Formamide.

Iodyl formamide was prepared in the same manner as iodyl acetamide. After purifying from chloroform the product had a melting point of 95° C. In pyridine silver iodide formed entirely on the cathode. Precipitation took place faster than in the case of iodyl acetamide. No precipitate formed on the anode. A similar color change was noted around the cathode.

Iodyl Propionamide.

Iodyl propionamide was prepared in the same manner as iodyl acetamide. After washing with chloroform the product had a melting point of 128° C. In acetonitrile, silver iodide was formed on both electrodes. In pyridine, silver iodide first formed on the cathode, and finally after several hours also on the anode. After ten hours the amounts formed on each electrode were approximately equal. Analysis gave: anode 53.12 per cent iodine; cathode 51.27 per cent iodine; calculated 54.06 per cent iodine.

Iodyl n-Butyramide.

This compound was prepared for the first time. The same method was employed as for iodyl acetamide. It was purified from butyramide and free iodine by washing with chloroform. It is a white solid with a melting point of 97° C., at which temperature it showed signs of decomposition. On analysis it gave 59.3 per cent iodine; calculated 59.6 per cent.

Iodyl n-butyramide immediately decomposes with water, precipitating free iodine. It is insoluble in chloroform and benzene, slightly soluble in ether, and soluble in alcohol, acetone and ethyl acetate. Electrolysis in pyridine took place more slowly than with iodyl propionamide. Both electrodes were eventually covered with silver iodide, the precipitate first

forming on the cathode as before.

Bromyl Propionamide.

Bromyl propionamide was made in the same manner as bromyl acetamide. After recrystallizing from absolute ether it was obtained as straw colored needles, melting at 80° C. A reddish stringy precipitate formed on the cathode in pyridine solution, and this precipitate was found to contain bromine.

Chloryl Succinimide.

Chloryl succinimide was prepared according to Bender (17) from bleaching powder and dilute acetic acid on succinimide. In pyridine solution a precipitate formed on the cathode and a very small crystalline precipitate on the anode. Chlorine was found in the cathode precipitate, and the anode precipitate was shown to be silver succinimide.(4) This is the first recorded case of cathodic chlorine, previous work giving cathodic bromine and iodine only.

Bromyl and Iodyl Succinimides.

Clark and Ball (4) investigated the electrolysis of these compounds in acetonitrile and other solvents. In pyridine, the present authors found that silver bromide and silver iodide, respectively, were formed on the cathode. On the anode a small amount of silver succinimide was formed. The cathodic solution in each case deepened in color.

Dichloryl Urea.

Dichloryl urea was prepared according to Chattaway.(18) It was washed with dry chloroform and dried in a vacuum desiccator for several hours over phosphoric anhydride. It had a melting point of 83° C. At the same time it decomposed to give nitrogen trichloride. On standing in the air it also gradually decomposed.

Chattaway noted its chemical properties were similar to those of nitrogen trichloride, which has been shown to contain positive chlorine.(19) In pyridine, a sticky red precipitate formed on the cathode, and bubbles of gas were also evolved at the same electrode. No precipitate or gas was formed on the anode. The cathodic precipitate contained chlorine.

Chloryl Phthalimide.

This compound was prepared according to Bredt and Hof.(20) It was recrystallized in white needles from benzene, and had a melting point of 182° C., but began to soften at 170°. No cotton plug was used in electrolysis. In absolute ethyl alcohol and dry nitromethane, silver chloride formed on the anode. An acetonitrile solution became slightly turbid on electrolysis, and a stringy precipitate formed only on the cathode.

In pyridine, a precipitate also formed on the cathode. Both precipitates were found to contain chlorine.

Bromyl Phthalimide.

Bromyl phthalimide was prepared according to the method of Bredt and Hof.(20) It was recrystallized from dry benzene in beautiful needles, which began to melt at 181° C. A cotton plug was not used, as the pyridine solution was a poor conductor. After ten hours a small precipitate formed on the cathode which was found to contain bromine.

Bromyl and Chloryl Benzamide.

Bromyl benzamide was made according to Linebarger (21) and recrystallized from benzene as a white powder, melting point 171° C. Chloryl benzamide was prepared from the bromyl compound by treating with hydrochloric acid,(21) and after recrystallizing from benzene had a melting point of 113° C. Both compounds were very poor conductors. In pyridine, small precipitates were formed on the cathode after twelve hours, which were found by analysis to contain the corresponding halide. No precipitates were deposited on the anode.

DISCUSSION OF RESULTS.

Further evidence for the existence of electromers in solution has been obtained. To account for the existence of such isomers, the electron bond theory must assume the movement of the bonding pair from the proximity of the halogen atom to that of the nitrogen atom, giving a halogen cation in certain solvents, and vice versa giving a halogen anion in other solvents. This might be more simply expressed by the plus and minus signs of the electronic formulae.

The conductivities of the various aliphatic iodyl amides decreased in the following order: Formamide > Acetamide > propionamide > n-butyramide. The latter two compounds deposited halogen on the anode as well as on the cathode, approximately at the same rate. An explanation is suggested by the theory of electron displacement. It is generally recognized (22) that alkyl groups are more positive than hydrogen, the accepted order of electron attraction being $H > CH_3 > C_2H_5 > C_3H_7 > C_4H_9$. The hydrogen of iodyl formamide has a stronger attraction for the bonding pair between it and nitrogen than has the methyl group in the corresponding union in iodyl acetamide.

Lewis (11) was the first to point out that the electron displacement, due to any substituent at one end of a chain of atoms, extends throughout the entire chain. Accordingly, the iodine in iodyl formamide would be more positive than the iodine in iodyl acetamide and hence would be a better conductor. Likewise, the iodine in iodyl acetamide would be more positive

than the iodine in iodyl propionamide or n-butyramide.

Iodyl formamide is very unstable, owing to the high degree of positivity of the iodine, replacing a positive hydrogen of the animo group. Iodyl acetamide is more stable, the positivity of the halogen atom being less, and now approaching that of the hydrogen atom.

The corresponding iodyl derivatives of the higher amides are unknown, probably because of a decrease in the positivity of the halogen, which is no longer able to replace a positive hydrogen of the animo group. Several attempts to prepare iodyl n-valeramide in this laboratory were unsuccessful.

Of all the solvents employed only pyridine and acetonitrile, gave cathodic halogen. Both solvents are given to forming addition products. The former has a low dielectric constant ($12.4^{21°}$), and the latter a fairly high one ($35.8^{20°}$). Levi and Voghera (23) electrolyzed a solution of potassium iodide in pyridine between platinum electrodes, and recovered hydrogen and a gray precipitate, found to contain C_5H_4NK, at the cathode. Free iodine was formed at the anode. On repeating the experiment between silver electrodes, iodine deposited on the anode as silver iodide. The cathode precipitate gave no test for halogen.

I wish to acknowledge the assistance of Dr. Clark and Mr.H.R.L.Streight in the preparation of this paper.

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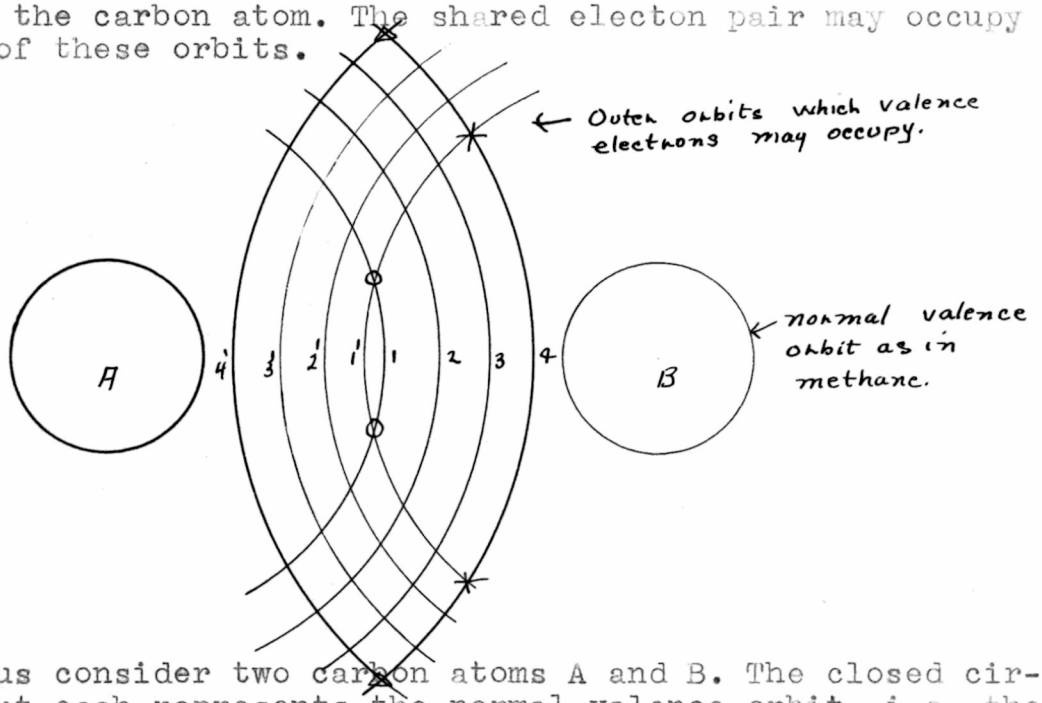
PART III

THE PREPARATION AND STUDY OF THE TWO ELECTROMERS OF 2-PENTENE.

According to the Lewis-Lucas electron displacement theory(1) the shared electron pair in a non-polar compound is situated midway between the two atoms. In a polar compound the shared electron pair is displaced toward the more electronegative atom. When the more electronegative atom assumes full possession of the electron pair ionization takes place.

Kharasch(2) in a recent modification of Lewis' theory considers that there are orbits outside the normal valence orbit of the carbon atom. The shared electon pair may occupy any two of these orbits.



Thus consider two carbon atoms A and B. The closed circles about each represents the normal valence orbit, i.e. the orbit of the eight valence electrons of methane.

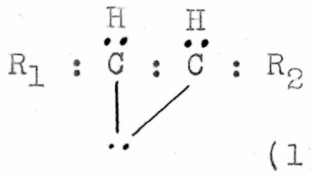
1,2,3,4, represent outer orbits of atom A, and 1',2',3', 4' outer orbits of atom B.

The electron pair may share an inner orbit of A and the corresponding inner orbit of B, i.e. orbits 1 and 1'. The shared electron pair is thus midway between the two carbon atoms. This would be a non polar bond.

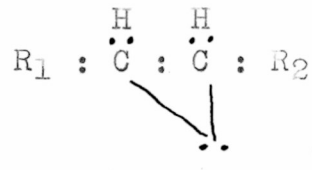
If A, due to radicals attached to it, is more electronegative than B, then the electron pair may share an inner orbit of A and an outer orbit of B, i.e. 1 and 4'. The electron

pair is now displaced from a position midway between the two atoms A and B. This position corresponds to a polar union.

In the case of the double bond in compounds of the ethylene series there are four shared electrons, or two electron pairs. Kharasch considers that one of these pairs is midway between the two carbon atoms, and that the second electron pair is displaced from an intermediate position.(3) He writes the electronic formulae for compounds of this type as follows:



(1)



(2)

showing the displacement of the second electron pair from the normal valence orbit.

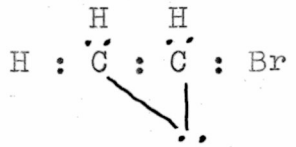
Whether (1) or (2) is the correct formula will depend on the relative electronegativity of the groups R_1 and R_2.

Take for example vinyl bromide:

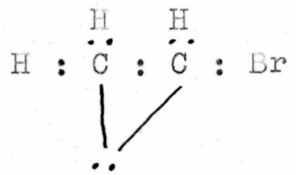
$$CH_2{=}CHBr.$$

The second electron pair will be displaced towards the most electronegative carbon atom, that is, the carbon atom that has the strongest pull on electrons. The question is, which carbon atom is the more electronegative?

According to the Lewis and Lucas theory the substitution of an electronegative atom for a hydrogen atom increases the electronegativity of the group, or carbon atom. That is, the =CHBr group will be the more electronegative. Hence the formula will be:



According to Kharasch, the substitution of an electronegative atom for a hydrogen atom decreases the electronegativity of the group, or carbon atom. That is, the CH_2 group will be the more electronegative. Hence the formula will be:



The question then involves determining who is right in regard to relative electronegativity of groups.

The series accepted by Lewis and Lucas is:

$$CBr_3 > CHBr_2 > CH_2Br > \varphi > H > CH_3 > C_2H_5 > C_3H_7$$

$\longleftarrow$ electronegativity

The series which Kharasch suggests is:

$$\varphi > CH_3 > C_2H_5 > C_3H_7 > \text{-----}H > CH_2Br > CHBr_2 > CBr_3$$

$\longleftarrow$ electronegativity

Lewis bases his series on the dissociation constants of the corresponding acids. Formic is stronger than acetic, etc. Kharasch points out that then benzoic acid should be stronger than formic, which is not the case. This exception invalidates the method.

Kharasch bases his series on:

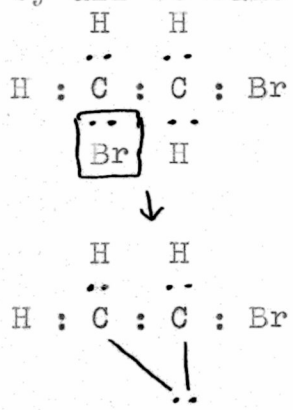
(a) Relative electronegativity as determined by the addition of mercury dialkyl to HCl. (4)

$$R_1HgR_2 + HCl \longrightarrow R_1HgCl + R_2H.$$

where R_2 is more electronegative than R_1.

(b) The addition of unsymmetrical reagents i.e. HBr to the ethylene double bond in compounds of the type in question.

The formation of unsaturated compounds from the corresponding alkyl halides by elimination of halogen acid is agreed by all to take place as follows:

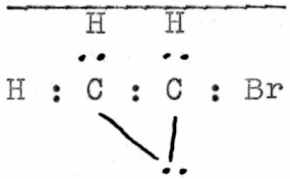


---the bromine atom taking the electron pair with it and the hydrogen dropping off to retain neutrality of the molecule.

Hence take for example the addition of HBr to Vinyl bromide.

Lewis Formula. Kharasch Formula.

Lewis Formula.



+ HBr

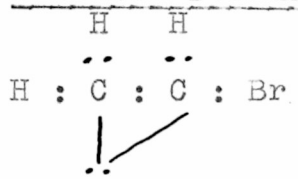
↓

CH_2BrCH_2Br

ethylene di-bromide

No such compound obtained.

Kharasch Formula.



+ HBr

↓

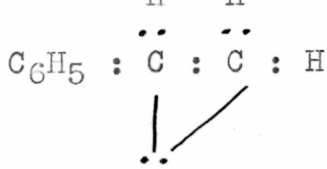
CH_3CHBr_2

ethylidene bromide

This is the compound formed.

Similarly Styrene.

Lewis Formula.



+ HBr

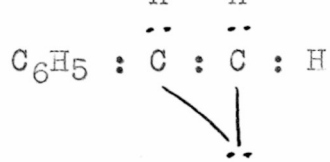
↓

$C_6H_5CH_2CH_2Br$

phenyl ethyl bromide

No such compound formed.

Kharasch Formula.



+ HBr

↓

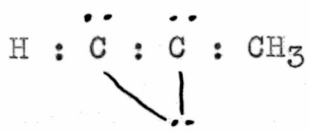
$C_6H_5CHBrCH_3$

Brom ethyl benzene.

This is the compound formed.

Also B chlor propylene, $CH_2{=}CCl{-}CH_3$.

Lewis Formula.



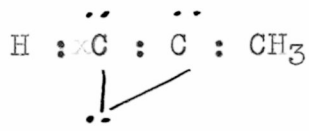
+ HI

↓

$CH_2ICHClCH_3$

No such compound formed.

Kharasch Formula.



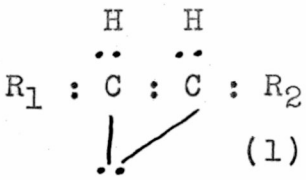
+ HI

↓

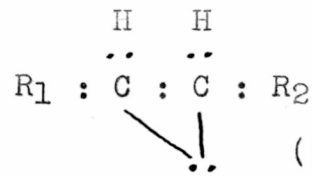
$CH_3CICICH_3$

Correct compound recorded.

Kharasch concludes that this is proof enough in favor of his series of electronegativity of radicals, and hence proof of the validity of his formulae for unsaturated compounds of the above type.



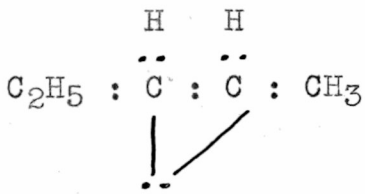
(1)



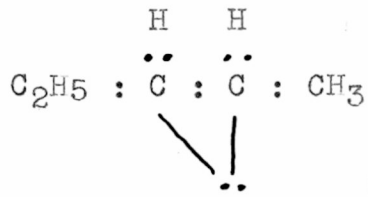
(2)

When R_1 and R_2 differ only slightly in electronegativity there is the possibility of both (1) and (2) existing.

For example: <u>2-Pentene</u>.



(1)



(2)

According to Kharasch 1 is the stable form and 2 is the matastable isomer. Since, however, C_2H_5 and CH_3 differ very slightly in electronegativity, it is very likely that 2 might also exist.

The metastable electromer has been prepared by Lucas and Moyse(5) and by Sherrill and co-workers(6) from 3-Bromo pentane.

Sherrill also prepared the stable electromer from 2-Bromopentane and compared some of the physical properties of the two isomers.

The physical properties are almost identical for the two isomers, as shown:

	B.P.(760 mm.)	d_4^{20}	n_D^{20}
2-Pentene (stable) from 2-bromopentane	35.85	.6481	1.37849
2-Pentene (metastable)--3-bromopentane	36.40	.6503	1.37965

In some chemical properties , however, they differ strikingly.

The stable variety adds HBr to form 2-bromopentane. The unstable electromer adds HBr to form 3-bromopentane.

The bromopentanes cannot be separated by distillation, as their boiling points(118.5 and 117.5) are too close to-gether. Their refractive indices,however, differ.

N_D^{20} for 3-bromopentane is 1.4443.

N_D^{20} for 2-bromopentane is 1.4416.

Lucas and Moyse(5) have shown that the refractive index of a mixture of 2-bromo and 3-bromopentanes is a linear function of the composition. Hence a mixture of the two electromers of 2-Pentene may be analysed by titrating with HBr and taking the refractive index of the resulting mixture of bromopentanes.

Kharasch and Darkis(3) and Sherrill(6) have shown that the unstable electromer of 2-Pentene (prepared from 3-bromopentane) in a non polar solvent such as CCl_4 etc. or without a solvent adds on HBr to form 98% 3-bromopentane and 22% 2-bromo pentane.

On treatment with heat or ultraviolet light,or sunlight for extended periods of time it forms as high as 85% 2-bromopentane, showing a transfer from the unstable electromer to the more stable form.

The stable electromer (2-Pentene from 2-bromopentane) on the other hand always gave 100% 2-bromopentane on addition of HBr. It was not affected by heat, ultraviolet light, etc.

It was the purpose of this investigation to synthesize the two electromers of 2-Pentene and make a further study of some physical properties, i.e. melting points. Electromers of some aromatic compounds show a marked and peculiar difference in melting points(7). It would be interesting to observe if there is likewise a difference in the melting points of the electromers of 2-Pentene.

The effect of magnetic and electrostatic fields on each of the electromers were to be studied, and in this way one might be able to offer additional proof for or against the existence of electromers.

SYNTHESIS OF THE ELECTROMERS.

A brief comparative summary of the syntheses is as follows:

2-Pentene (stable)	2-Pentene (unstable)
	Sodium formate
	($EtHSO_4$)

comparative summary of synthese--continued.

acetaldehyde	ethyl formate
↓ (Grignard synthesis) C_3H_7MgBr	↓ (Grignard synthesis EtMgBr)
methyl normal propyl carbinol	diethyl carbinol
↓ (HBr)	↓ (HBr)
2-bromopentane	3-bromopentane
↓ (KOH)	↓ (KOH)
2-Pentene (stable)	2-Pentene (unstable)

Synthesis of 2-Pentene (unstable electromer).

$$\underset{\text{Formic Acid}}{H\text{-}COOH} + NaOH \rightarrow HCOONa$$

$$\underset{\text{Sodium formate}}{HCOONa} + EtHSO_4 \rightarrow H\text{-}COOEt + NaHSO_4$$

$$\underset{\text{Ethyl formate}}{H\text{-}COOEt} + EtMgBr \longrightarrow H\text{-}C(OMgBr)(Et)(OEt)$$

$$H\text{-}C(OMgBr)(Et)(OEt) + EtMgBr \rightarrow H\text{-}C(OMgBr)(Et)(Et) + EtOMgBr$$

$$H\text{-}C(OMgBr)(Et)(Et) + H_2O \rightarrow H\text{-}C(OH)(Et)(Et) + MgBrOH$$

$$\underset{\text{Di-ethyl Carbinol}}{(Et)_2CHOH} + HBr \rightarrow CH_3\text{-}CH_2\text{-}CHBr\text{-}CH_2\text{-}CH_3$$

$$CH_3\text{-}CH_2\text{-}CHBr\text{-}CH_2\text{-}CH_3 + KOH \longrightarrow CH_3\text{-}CH_2\text{-}CH : CH\text{-}CH_3$$

2-Pentene (unstable)

<u>Sodium formate.</u>

Sodium formate was prepared by adding the calculated amount of sodium hydroxide solution to formic acid, and eva-

porating to dryness at a fairly low temperature.

Ethyl formate.

Ethyl formate was prepared by adding concentrated sulphuric acid(6.8 moles) to ethyl alcohol (6 moles) and then adding slowly sodium formate (6 moles). The reaction mixture was kept below 30° with ice and salt. If it heated itself above this temperature the reaction became so violent that all the ethyl formate was volatalized. The reaction mixture was allowed to stand over night, and then the ethyl formate was distilled off. It was washed with water and sodium carbonate solution, dried with calcium chloride and distilled. It distilled at a constant boiling point of 54.7°C.(755mm.)

Diethyl Carbinol.

This was prepared by a Grignard synthesis from ethyl bromide and ethyl formate. Ethyl magnesium bromide was prepared according to the method of Wood and Scarf(9). 195 gms. of magnesium turnings were placed in a 5 litre flask with 500cc. of ether. A little copper magnesium alloy was added as accelerator. Then 30 gms. of ethyl bromide were added. As soon as the reaction started, the flask was placed in an ice and salt freezing mixture, and was fitted with a cork having an airtight valve (see description by Wood and Scarf) through which a stirring rod passed. A calcium chloride tube was attached; also a dropping funnel. 800 c.c. of ether were now rapidly added, the mechanical stirrer was started, and the remaining ethyl bromide (840)gms.) was added drop by drop through the dropping funnel over a period of 4 or 5 hours, the reaction mixture being stirred continuously with the mechanical stirrer.

These elaborate precautions were taken in order to minimize the risk of the formation of hydrocarbons, i.e.:

$$2EtBr + Mg \rightarrow MgBr_2 + Et\text{-}Et.$$

a reaction which reaches large proportions when the ethyl bromide is added too quickly, and local heat of reaction is developed. The flask was protected from the moisture of the air to prevent reaction with the Grignard reagent.

After making sure that the above reaction was complete, 300 gms. of ethyl formate were added by means of the dropping funnel, drop by drop, over a period of 4 hours. The flask was kept cold, as before, and the mixture stirred continuously.

The contents of the flask were treated in small portions with ice and water. HCl was added to decompose the magnesium hydroxide formed. The ether layer (containing the carbinol) was separated from the water layer, dried, and the ether distilled off. The diethyl carbinol was fractionated through a lagged Hempel column. The fraction boiling at 114-115.5° was collected.

It had a refractive index , N_D^{20} 1.4100 .

3 Bromopentane.

The above compound was prepared by the action of hydrogen bromide on diethyl carbinol.

Hydrogen bromide was generated by the action of bromine on naphthalene covered with a layer of kerosene. The gas was freed from bromine by bubbling through wash bottles containing red phosphorous and 48% hydrobromic acid, dried by passing through an anhydrous sodium sulphate tube, and finally passed into the flask containing the diethyl carbinol kept at -10° by a freezing bath.

On saturation the flask was fitted with a stopper to which a toy rubber balloon was attached. The reaction mixture was allowed to warm up to room temperature. On collapse of the balloon, indicating complete adsorption of the hydrogen bromide, the flask and contents were again cooled to -10° and hydrogen bromide bubbled in again. This process was repeated till no more hydrogen bromide was adsorbed. Lucas and Moyse(5) in preparing the compound, heated the diethyl carbinol(after adsorption of hydrogen bromide at a low temperature) to 60° under pressure. Sherril(8) heated to 60° but with no pressure.

After lengthy experimentation it was found that when the above methods were used, the product was a mixture of 3-bromopentane and 2-bromopentane. As the slightest trace of 2-bromopentane (detected by the refractive index of the product---- 1.442-- instead of 1.4443) could not be tolerated, we were forced to use the procedure first mentioned, namely, saturation of the diethyl carbinol at low temperatures, allowing the reaction mixture to warm to room temperature and under atmospheric pressure only.

When complete saturation was reached (50-60 hrs.) the product was washed with water, with 48% hydrobromic acid, sodium carbonate solution, again with water, and finally dried with potassium carbonate. On distillation (B.P. 117.8-118.5) the 3-bromopentane had a refractive index of N_D^{20} 1.44429 (Bausch and Lombe dipping refractometer).

Lucas and Moyse, and Sherrill used concentrated sulphuric acid instead of 48% hydrobromic acid in washing the product. We found that such treatment tends to develop decomposition of the bromide; it acquires a pink tint and hydrobromic acid is given off on distillation. McCullough and Cortese(10) recommend the use of 48% hydrobromic acid and Sherril herself has in later work substituted it for sulphuric acid(11).

2-Pentene (unstable).

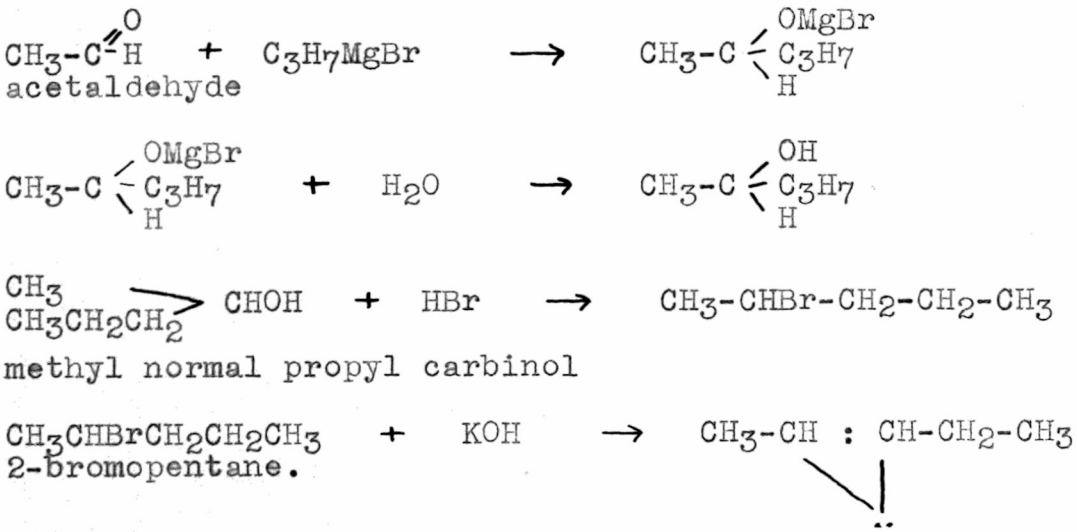
-----see next page-page22.

2-Pentene (unstable isomer)

The electromer was prepared by treating 3-bromopentane with alcoholic potash(12).

3-bromopentane was dropped slowly into a solution of potassium hydroxide in absolute methyl alcohol heated on an oil bath kept at 110-115°. The methyl alcohol was refluxed by a condenser kept at 40°, the 2-pentene (B.P. 35°) passed through and was condensed in a cold downward condenser and collected in absolute methyl alcohol. The azeotropic mixture was fractionated through a lagged hempel column. The temperature remained constant at 31.8° till all the 2-pentene was distilled over, and then shot up to 65°. The 2-pentene was separated from methyl alcohol by washing with water. It was dried with calcium chloride and distilled; N_D^{20} 1.3798 . B.P. 36.5°C.

Synthesis of 2-pentene (stable isomer) (13)



Methyl normal propyl carbinol.

This compound was prepared following the directions as given in detail by Wood and Scarf(9). B.P. of final product was 118.2--119.6° (755mm) N_D^{20} 1.40602.

2-bromopentane.

The method used for 3-bromopentane was employed.(8). The precautions employed in the preparation of 3-bromopentane were not quite as necessary, as the 2-bromopentane was much easier to prepare. B.P. 117--118°(755mm.) N_D^{20} 1.44125

2-pentene (stable)

The stable electromer was prepared from 2-bromopentane by the action of alcoholic potash. Details were the same as

in the case of the preparation of the unstable electromer from 3-bromopentane. As there was here the possibility of some 1-pentene forming, the azeotropic mixture with alcohol was fractionated very carefully. The fraction boiling above 30.1° was collected. B.P. 35.8° (755mm). N_D^{20} of the final product was 1.37845.

MELTING POINTS

The melting points of the isomers were obtained using a standardized platinum resistance thermometer. A bath of super-cooled 2-pentene (Eastman Kodak) was used suspended over liquid air so that the temperature could be regulated to within a tenth of a degree. The electromer whose melting point was to be determined was placed in a small glass bulb which could be shaken to stir the contents and at the same time served to stir the outside bath. The electromer was crystallized by placing the bulb in liquid air, then warming it up, then placing it in liquid air again, and finally placing it in the bath of supercooled 2-pentene, where sometimes after 10 or 15 minutes a small crystal would form. By shaking the contents of the bulb the crystal broke in a number of smaller pieces, more crystals grew, and finally the contents of the bulb froze solid.

The temperature of the pentene bath was raised slowly and the melting point temperature noted. The temperature at which crystals neither formed nor disappeared was taken as the melting point. The amount of supercooling for 2-pentene is usually about 30-40°.

The melting point for 2-pentene given in the International critical tables is -139°C.

The value obtained by Gill and Seyer(14) for 2-pentene was -149°C.

The values we obtained for the two electromers are as follows:

unstable electromer-- -144°C.
stable electromer-- -149°C.

The figures for the two electromers are as yet only tentative and have to be confirmed by further work.

The effect of magnetic and electrostatic fields on the electromers has not as yet been determined. Difficulties in the synthesis of the electromers to date have prevented a large enough quantity of each being prepared. The work is being continued.

In conclusion I wish to express my most sincere thanks to Dr. Clark for valuable aid and advice received throughout all this work.

E.G. Hallonquist.

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(3) For further proof of this statement see article quoted above.

(4) Kharasch and Marker, J.Am,Chem.Soc., 48, 3130 (1926).

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