

SOLVENT EFFECTS ON THE IONIC DECOMPOSITION OF
t-BUTYLPEROXYFORMATE. AN EMPIRICAL CORRELATION
OF RATE WITH SOLVENT PROPERTIES

by

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B.A., University of Colorado, 1962

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department

of

Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1965

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ABSTRACT

Rate constants for the pyridine catalyzed ionic decomposition of t-butylperoxyformate (TBF) are measured in 15 non-hydroxylic solvents. The second order rate constants varied by a factor of 40 from the "slowest" solvent, tetrachloroethylene, to the "fastest", 1,2-dichloroethane. Ten different empirical equations are found and their ability to correlate the rate constants with bulk solvent properties is compared. The best of the ten equations involves the polarizability and dipole moment of the solvent as follows.

$$\log k^{\text{rel}} = 1.207 \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) + 3.99 \mu + 0.003 - 3$$

The rate constants for TBF decomposition in other non-hydroxylic solvents are calculated by the empirical equations and are compared with values previously reported. The average deviation of the log k is 0.22. The rate constants for the reaction of methyl iodide with triethylamine are calculated from solvent properties and the values compared to literature values. In this case the average deviation of the log k is 0.31.

ACKNOWLEDGEMENT

I would like to thank Dr. R. E. Pincock for his help and encouragement throughout the course of this work. I also wish to thank the National Research Council, the University Research Committee and the staff of the UBC Computing Center.

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INTRODUCTION

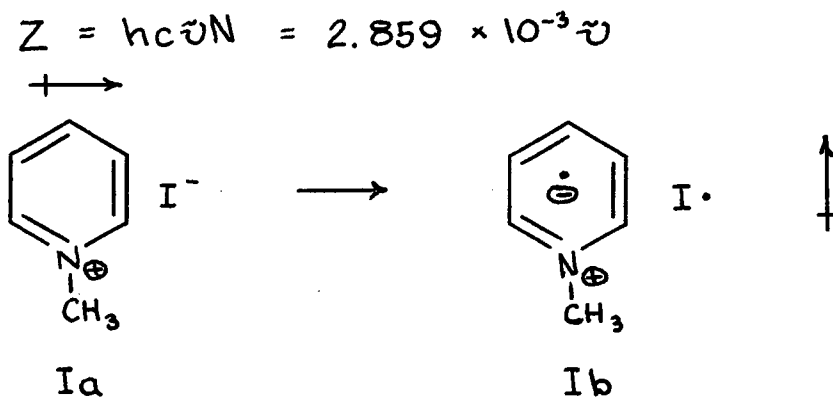
Various proposals^{1,2,3,4,5} have been made over the years for means of correlating reaction rates with the solvents in which the reactions are carried out. One rather successful proposal, developed by Kirkwood¹, for application to dipolar or ionic reactions is based on theoretical considerations alone. Kirkwood has given for the free energy change for transfer of a strong dipole of moment μ from a vacuum to a continuous medium of dielectric constant D an expression which, when the charge distribution within the molecule is symmetrical, becomes,

$$\Delta F = - \frac{\mu^2}{a^3} \left[\frac{D-1}{2D+1} \right]$$

Since polar solvents increase the rate of a reaction in which the transition state is more polar than the initial state, this dielectric constant function, $\frac{D-1}{2D+1}$, should be directly proportional to the logs of the rate constants..

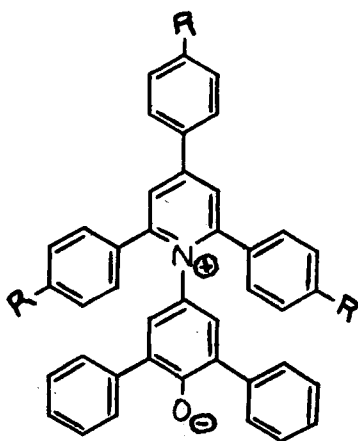
A number of empirical proposals for correlation of rates of dipolar reactions have also been made. Kosower² has proposed using the charge-transfer transition energy between states of some 1-alkyl-pyridinium salts as a measure of solvent polarity. The transition is between states represented by Ia and Ib. He called the molar transition

energies, calculated from the position of the absorption maxima, "Z" values. Kosower calculates the dipole moment



of Ia to be 13.9D and that of Ib to be 8.9D. Since there is a fairly large change in dipole moment the ease of transition should be sensitive to the polarity of the solvent. The main difficulty with this proposal is that these complexes are insoluble in any but highly polar solvents. The least polar solvent for which he was able to obtain a "Z" value was chloroform.

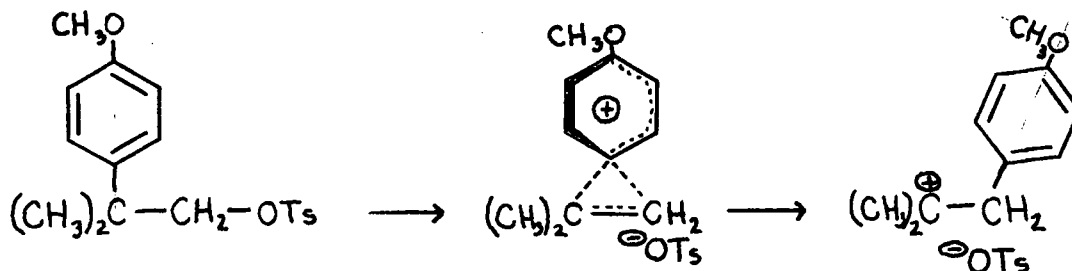
Dimroth, Reichardt, Siepmann, and Bohlmann^{23,24} have proposed using the molar transition energy, E_T , calculated in the same way as "Z" values, of a pyridinium N-phenolbetaine II or III as an empirical measure of solvent polarity. This compound has the advantage that the shift of the absorption maximum is large upon changing solvent and III is soluble in hydrocarbon solvents. These authors have obtained E_T values for 62 solvents and five solvent mixtures.



II: R=H

III: R=CH₃

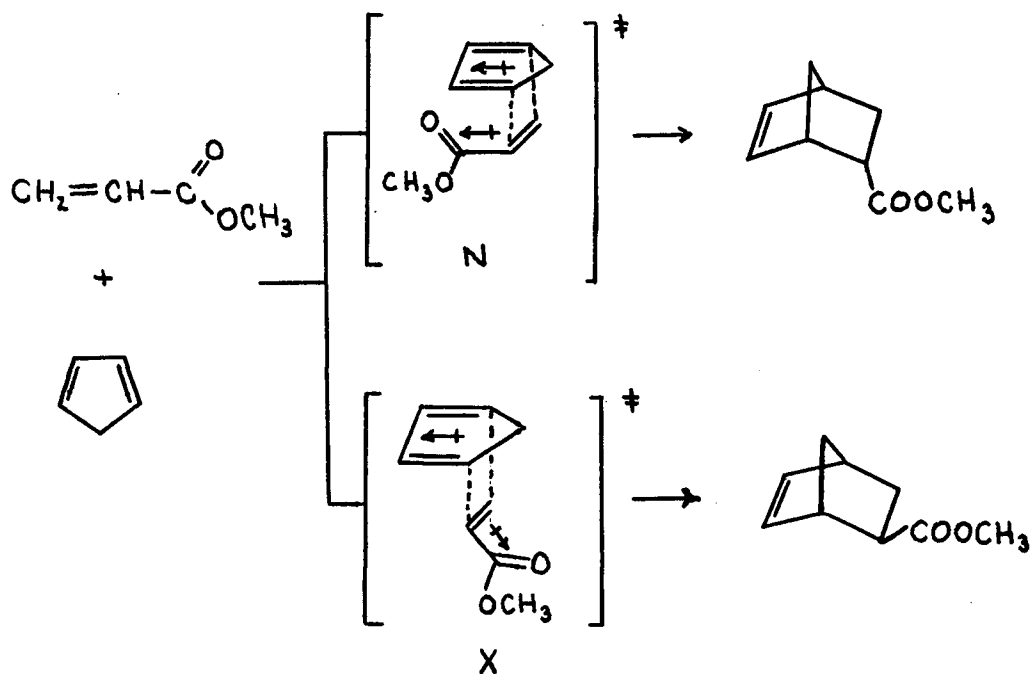
Smith, Fainberg and Winstein³ have measured the rate of ionization of p-methoxyneophyl toluenesulfonate in various solvents and propose the log of this rate constant as a measure of solvent polarity. This reaction has the advantage



of being measurable in both hydroxylic and non-hydroxylic solvents. A plot of $\log k_{ion}$ versus $\frac{D-1}{2D+1}$ gives a rough straight line if hydroxylic solvents are omitted, while a plot of $\log k$ versus Z values gives a rather good straight line. In some solvents, benzene for instance, autocatalysis takes place and k_{ion} varies with the extent of reaction.

A parameter, Ω , defined as the log of the ratio of the

per cent endo to exo adduct in the reaction between cyclopentadiene and various dienophiles is proposed as a measure of solvent polarity by Berson, Hamlet and Mueller⁴. The arrangement, N, which leads to endo product would be favored



by polar solvents more than the arrangement X, which leads to exo products. The $\log\left(\frac{N}{X}\right)$ should then be sensitive to solvent polarity. A plot of Ω versus Kosower's Z values is a rather good straight line, the correlation being about as good as that between k_{ion} and Z.

Grunwald and Winstein⁵ proposed in 1948 their famous linear free energy relationship for correlating solvolysis rates.

$$\log \frac{k}{k_0} = mY$$

k is the rate constant for solvolysis of a compound in any solvent, k_0 is the rate constant for solvolysis in the standard solvent (80% aqueous-ethanol), m is a measure of the sensitivity of the substrate to changes in the solvent and Y is a measure of the ionizing power of the solvent. The fact that plots of logs of the rate constants in different solvent pairs give different lines indicates that more than one property of the solvent is involved in determining the rate⁶.

In order to overcome this difficulty Winstein, Grunwald and Jones⁷ developed a two parameter equation in which Y is a measure of solvent ionizing power and N is a measure of the nucleophilicity of the solvent. The partial differential

$$d \ln k = \left(\frac{\partial \ln k}{\partial Y} \right)_N dY + \left(\frac{\partial \ln k}{\partial N} \right)_Y dN$$

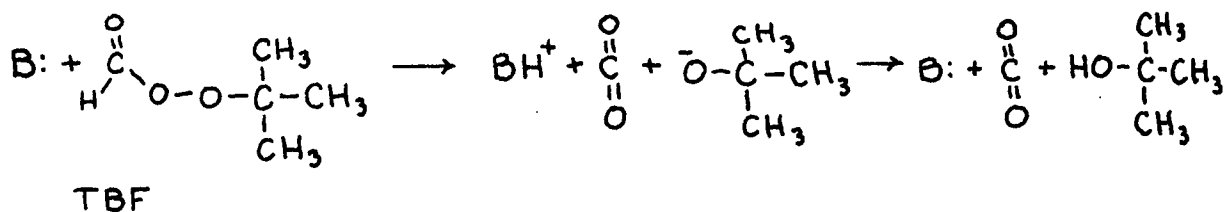
quantities were estimated by measuring the change in $\ln k$ when Y was changed but N was constant and when N was changed but Y was constant.

A similar approach is possible using any combination of properties of the solvent. In order to correlate and predict the rates of dipolar reactions in various solvents, I have attempted to set up an equation similar to Winstein's but using physical properties of the solvent instead of the vague properties of nucleophilicity and ionizing power. The

partial differential quantities were determined in my treatment by multiple regression analysis carried out on an IBM 7040 computer. The potential value of such a treatment is summed up by Laidler⁸ in the following quotation.

Empirical relationships may be useful in allowing reliable estimates to be made of the properties of systems for which no experimental data are available. Another and more important use of an empirical treatment is that it may lead to a valuable theoretical interpretation. It is important in developing an empirical treatment to have due regard to whatever theories are available in order that the empirical treatment be of most value.

The rate constants used in this investigation of solvent effects were those of the base catalyzed decomposition of t-butylperoxyformate (TBF). This decomposition goes through a very polar transition state and is easily studied in a wide variety of solvents. There are perhaps more data potentially available than there are for establishing Z, Ω , and k_{ion} (but not for E_T) discussed above. The mechanism for the base catalyzed decomposition of TBF has been established by Pincock⁹ and proceeds as shown. The highly polar transition state results from the charges formed being separated by the neutral CO_2 . This charge separation causes the reaction to be very sensitive to changes in solvent polarity.



RESULTS

The base catalyzed decomposition of TBF follows pseudo first order kinetics, since the base is regenerated and thus has a constant concentration.

$$\frac{d(\text{TBF})}{dt} = \text{Rate} = -k_2(\text{Base})(\text{TBF})$$

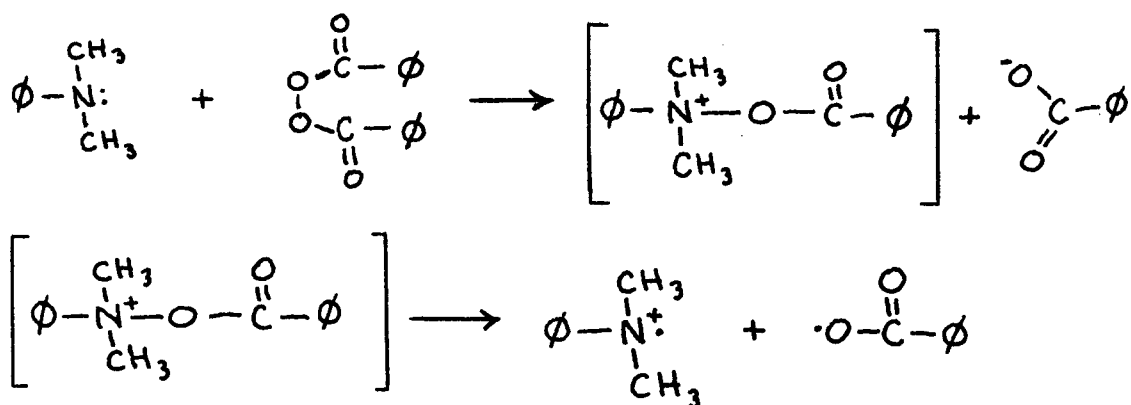
$$\int \frac{d(\text{TBF})}{(\text{TBF})} = -k_2(\text{Base}) \int dt$$

$$\ln(\text{TBF}) = -k_2(\text{Base})t + \text{const.}$$

$$\log \frac{(\text{TBF})_0}{(\text{TBF})} = \frac{+k_2(\text{Base})t}{2.303}$$

Since the decomposition was followed by measurement of the loss of infrared carbonyl absorption the function $\log \frac{A_\infty - A_0}{A_\infty - A}$ was plotted versus t in minutes, where A_∞ is the absorbance of a sample left for more than ten half lives, A_0 is the absorbance of the sample taken at $t = 0$ and A is the absorbance of a sample at any time. The first order plots were good straight lines followed usually to 80% decomposition with slope of $\frac{k_2(\text{Base})}{2.303}$. k_2 in l/mole sec. is found by dividing the slope by $(60)(\text{Base})$ and multiplying it by 2.303. The rate constants in various solvents found in this way are listed in Table I.

The decomposition of TBF can also proceed by a free radical chain mechanism, but Pincock⁹ has shown that the rate of thermal decomposition at 90° is slow. According to Walling¹⁰ free radicals are sometimes produced from polar transition states in amine peroxide reactions. For example radicals are produced in the reaction between phenyldimethylamine and dibenzoylperoxide.



In order to insure that no free radical chain decomposition was occurring in solvents from which oxygen had been removed by degassing, runs were made in solutions of about .02M quinone. Since the addition of quinone did not affect the rate, it was concluded that no such radical decomposition was taking place.

It was found that degassing of the solvent was necessary in some cases in order to get reproducible kinetics. The procedure used was to freeze the solution in a low temperature bath and allow it to melt under vacuum produced by a rotary vacuum pump. The ampoules were then refrozen and

sealed under vacuum.

Halogenated solvents may react with the pyridine used as a catalyst in TBF decomposition by elimination or displacement reactions. For example, it was noted during the course of this research that n-butylchloride reacts with pyridine even under the mild conditions used. In order to find out whether pyridine was reacting with the solvents runs were made at different pyridine concentrations. Since the second order rate constants, for solvents listed in Table I, did not change with changes in pyridine concentration it was concluded that there was no such reaction taking place. Rate constants for the base catalyzed decomposition of TBF are listed in Table I along with the number of runs made in the solvents and the average deviation from the mean.

An empirical correlation of the rate constants with various combinations of solvent parameters, the choice of which is explained in the discussion section, was made using an equation of the form,

$$\log k_2 = A(P_1) + B(P_2) \dots N(P_n) + \text{Const.}$$

P_1 represents some solvent parameter such as polarizability, P_2 some other parameter such as dipole moment and so forth. The coefficients A, B, etc. were determined using multiple regression analysis. This procedure results in a set of coefficients which minimize the error in $\log k_2$. It is further explained in the appendix.

TABLE I

Rate Constants for Decomposition of TBF in Various Solvents

Solvent	Notes	No. Runs	$k_2 \times 10^3$ l./molesec.
Tetrachloroethylene	a	2	4.89 ± 0.1
<u>trans</u> -Dichloroethylene	a,b	2	12.0 ± 0.0
1,1,1-Trichloroethane	a,b	4	20.2 ± 1.4
Trichloroethylene	a,b	2	22.6 ± 1.8
<u>p</u> -Dichlorobenzene	c	2	28.7 ± 1.7
Fluorobenzene		3	30.2 ± 1.1
<u>m</u> -Dichlorobenzene		3	37.6 ± 1.3
Chlorobenzene		3	46.6 ± 0.6
Bromobenzene		3	49.6 ± 0.7
Iodobenzene		2	63.2 ± 2.0
<u>cis</u> -Dichloroethylene	a,b	2	72.7 ± 0.6
<u>o</u> -Dichlorobenzene	a	2	75.8 ± 0.6
Tetrachloroethane	a	3	79.5 ± 6.7
1,1-Dichloroethane	a	2	105 ± 4.0
1,2-Dichloroethane	a,b	2	207 ± 3.0

a Degassed b Run with .02M quinone

c Aliquots taken instead of sealed tubes

In Table II are listed the values found for the coefficients under the parameter for which they were determined; for example, Equation 6 would read,

$$\log k_2^{\text{rel}} = -0.030 \left(\frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{\rho} \right) + .405(\mu) + .138(\Delta H_v) - 0.023 - 3$$

where k_2^{rel} is relative to k_2 for tetrachloroethylene. The actual $\log k_2$ is calculated by adding 0.69 to $\log k_2^{\text{rel}}$, since k_2 for tetrachloroethylene is 4.89×10^{-3} l/mole sec.

In Table III are listed the values of solvent parameters used to determine the coefficients. Unless otherwise noted the values were taken either from Weissberger¹¹ or from the "Handbook of Chemistry and Physics"¹².

TABLE II

Regression Coefficients For Ten Different
Combinations of Solvent Parameters

Eq. No.	$\frac{n_D^2 - 1}{n_D^2 + 2}$	$\frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{\rho}$	μ	b.p.	$\frac{M}{\rho}$	$\frac{\rho}{M}$	ΔH_v	$\frac{D-1}{2D+1}$	$\frac{1}{n}$	$\frac{\Delta H_v}{M/\rho}$	Const.
1	-4.708		0.376	0.004				0.154			1.282
2	-10.63		0.314	0.006	0.009						3.412
3		-0.306	0.462				0.154		-0.055		0.034
4		-0.043	0.475		0.004		0.161				-0.251
5		-0.001	0.472			95.52	0.145				-1.945
6		-0.030	0.405				0.138				-0.023
7		-0.108	0.552							10.28	-0.498
8	-0.496		0.550							9.54	-0.596
9	3.278							3.995			-1.541
10	1.207		0.399								0.003

TABLE III

Solvent Parameters Used In Computation Of
Regression Coefficients.

Solvent	M.W.	b.p.	n_D	μ	ρ	ΔH_V	D	η
Tetrachloroethylene	165.8	121.2	1.507	0.00	1.623	8.299	2.30	0.888
<u>trans</u> -Dichloroethylene	96.5	47.6	1.452	0.00	1.255	6.905	2.14	0.404
1,1,1-Trichloroethane	133.4	73.9	1.438	1.79	1.349	7.692	7.52	0.681
Trichloroethylene	131.4	87.2	1.477	0.90	1.468	7.521	3.42	0.566
<u>p</u> -Dichlorobenzene	147.0	174.1	1.528	0.00	1.247	13.6	2.41	1.01 ^a
Fluorobenzene	96.1	84.85	1.465	1.47	1.024	7.695	5.42	0.707 ^a
<u>m</u> -Dichlorobenzene	147.0	173.0	1.546	1.48	1.288	9.36 ^b	5.04	1.13 ^a
Chlorobenzene	112.6	132	1.525	1.56	1.106	8.735	5.70	0.799
Bromobenzene	157.0	155	1.562	1.73	1.495	9.049	5.40	1.090
Iodobenzene	204.0	188	1.621	1.80 ^c	1.832	9.90 ^b	4.63	1.02 ^a
<u>cis</u> -Dichloroethylene	96.95	60.36	1.449	1.89	1.282	7.225	9.20	0.467
<u>o</u> -Dichlorobenzene	147.0	180.4	1.551	2.26	1.306	9.48	9.93	1.16 ^a
Tetrachloroethane	167.9	146.2	1.497	1.85	1.595	9.236	8.20	1.715
1,2-Dichloroethane	98.97	83.5	1.448	2.06	1.252	7.654	10.36	0.835

a Calculated from the Papov equation $\eta = \left(\frac{s}{M/\rho}\right)^3$

Chem. Abstracts 54 6239h (1960)

b Calculated from Trouton's rule $H_V = 21T$

c The gas phase value of 1.80 was used instead of the liquid phase value of 1.27

DISCUSSION

In Table IV are listed values of $\log k_2$ for the decomposition of TBF along with Ω , Z , E_T and $\log k_{ion}$ for solvents in which data for both are available. The agreement with $\log k_2$ for TBF is best with $\log k_{ion}$, which is not surprising since both are rate constants for polar reactions. Unfortunately not enough data is available to make a really meaningful comparison except for E_T values.

The fact that the correlation between $\log k_2$ and E_T is not very good is no doubt because the solvent interacts differently with different substrates. Any treatment which relies on a measure of the interaction of the solvent with a certain substrate will suffer from this difficulty. The more similar the substrates in two treatments the greater will be the correlation. This result makes one wonder about the usefulness of trying to correlate rate data with such empirical measures of solvent polarity. For a comparison of all the parameters mentioned above except $\log k_2$ see Reichardt²³.

A plot of $\log k_2$ for the decomposition of TBF versus the Kirkwood function, $\frac{D-1}{2D+1}$, is shown in Figure 1. The plot yields a rough straight line with the exception of 1,1,1-trichloroethane. The reason for this solvent being so far off the line is probably that due to the odd shape of the molecule its dipole axis is prevented from becoming parallel to that of the TBF transition state. Since the plot in Figure 1 is

only a rough straight line there must be other factors which affect the rate constant.

The parameters used in the equations of Table II were chosen because it was felt these quantities had some chance of being related to properties of the solvents which affect the rates. The Kirkwood parameter is justified because it is so often used and seems to work fairly well. However, Wiberg¹³ states, "It is evident that dielectric constant is not a useful value for describing the effect of the solvent on a dipolar species except in certain special cases, such as a mixture of two solvents."

Many functions of the index of refraction are related to the polarizability of the molecule. $\frac{n_D^2 - 1}{n_D^2 + 2}$ was found by Pincock⁹ to correlate the rate of TBF decomposition fairly well in solvents with no permanent dipole moment. A similar function, $\frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{\rho}$, the molar refraction, was used because it is a measure of the deformability or polarizability of the electron clouds in a molecule¹⁴ in an electric field. It was thought that the transition state dipole would be stabilized by fields resulting from dipoles induced in the solvent molecules and the more polarizable the solvent molecules the greater the stabilization.

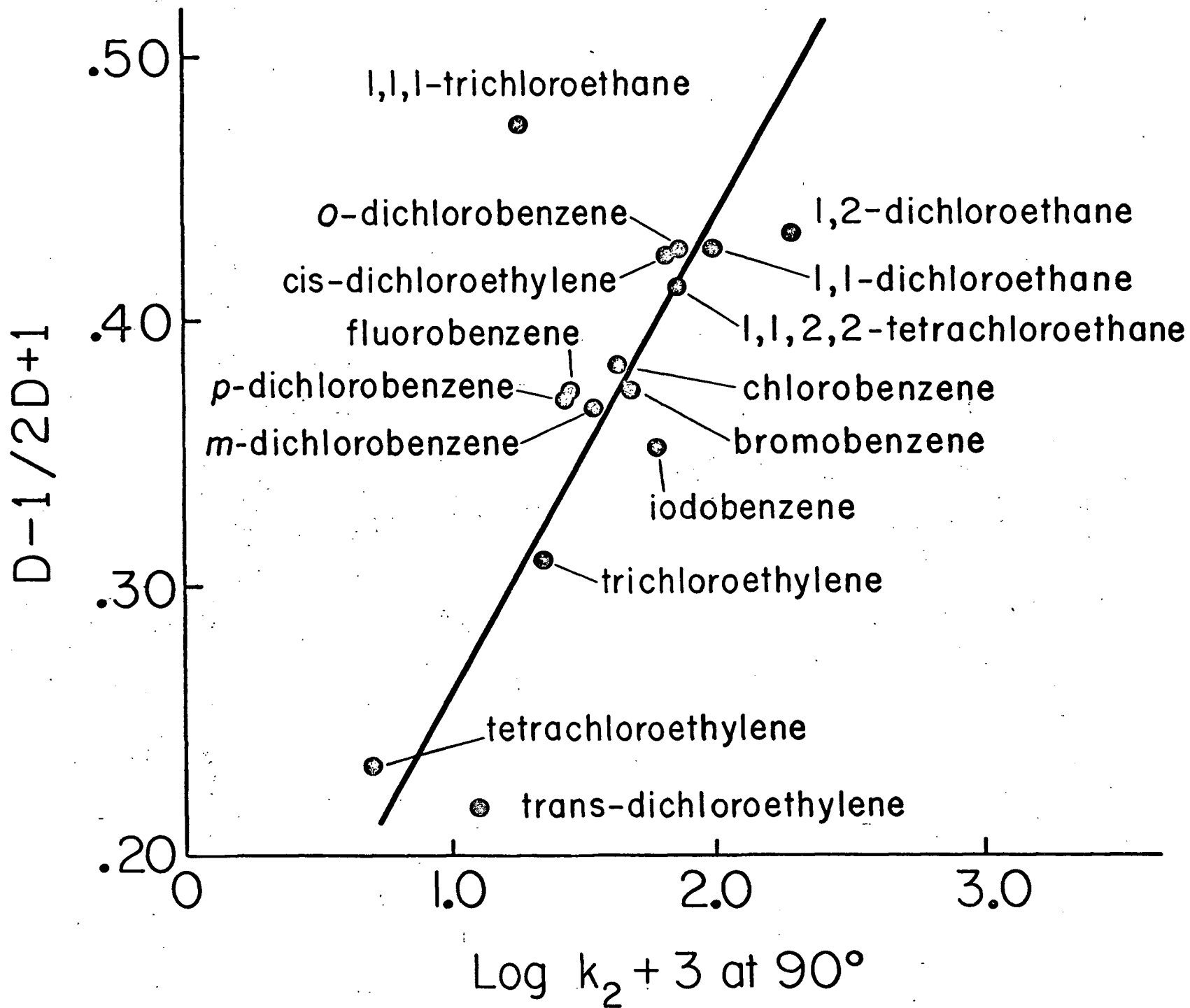
The boiling point was used because it is related to the latent heat of vaporization. The latent heat of vaporization is a measure of the energy of attraction between solvent molecules and so may be related to the ability of solvent

TABLE IV

Comparison of TBF Rate Constants with Various
Proposed Measures of Solvent Polarity

Solvent	$\log k_{2+3}$	Ω	Z	E_T	$\log k_{ion+7}$
1,2-Dichloroethane	2.32	0.552	63.2	10.37	
Nitrobenzene	2.32			34.6	
Nitromethane	2.22	0.642		38.57	3.08
Dichloromethane	1.84			8.9	
Acetonitrile	1.71	0.634	71.3	37.5	2.78
Bromobenzene	1.70			5.39	
Chlorobenzene	1.66			5.61	
Chloroform	1.66		63.2	4.70	
Tetrahydrofuran	1.45			7.39	0.93
p-Dioxane	1.36			2.21	
Benzene	1.33			2.27	
Toluene	1.25			2.38	
Carbontetrachloride	0.78			2.23	

Note: TBF rate constants not reported in this thesis
were taken from Pincock (Ref. 9).



molecules to solvate the transition state.

Direct dipole-dipole interaction between the transition state dipole and the dipoles of solvent molecules which have permanent dipole moments was thought to be an important factor. The magnitude of the interaction is given by $\frac{\mu_A \mu_B \cos \Theta}{r^3}$ ¹⁵, where r is the distance between the centers of the dipoles and Θ is the angle between them. The dipole moment of the transition state was assumed to be the same in all the solvents and $\cos \Theta$ was assumed to be a constant since there was no way of taking it into account. The rate should then be proportional to the dipole moment of solvent molecules and probably to r^3 .

It was hoped that the dependence of dipole-dipole interaction on r^3 could be accounted for by using molar volume or its reciprocal as a separate variable. The molar volume is defined as $\frac{M}{\rho}$. The larger the molar volume (the volume of a solvent molecule) the less should be the electrostatic interaction.

The molar volume was also used in a quantity called the internal pressure¹⁶, defined as $\left(\frac{\Delta E}{\Delta V}\right)_T$ which is approximately equal to $\frac{\Delta H_v}{M/\rho}$. The internal pressure of a liquid arises from the balance of attractive and repulsive forces between molecules of the liquid. It was thought that this quantity might be a good measure of the ability of solvent molecules to be packed around the transition state dipole.

The fluidity, the reciprocal of the viscosity, was used because it was felt that the ability of the solvent molecules to rearrange themselves to accommodate the newly formed transition state dipole might be proportional to it. The viscosity is also related to the latent heat of vaporization¹⁷.

The combination of parameters in the various equations was more or less arbitrary since it was impossible to tell beforehand what combination would give the best equation. The equations were tested by calculating the rate constants for TBF decomposition in solvents which had not been used in finding the coefficients. In Table V are listed the calculated rate constants both for solvents used in determining the coefficients and for others not used. The average deviation of the calculated values from the measured ones for the solvents not used in determining the coefficients is listed under each column.

In terms of average deviation Equations 9 and 10 are the best, having respectively average deviations of 0.23 and 0.22.

$$\text{Eq. 9} \quad \log k_2^{\text{rel}} = 3.278 \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) + 3.995 \left(\frac{D-1}{2D+1} \right) - 1.541 - 3$$

$$\text{Eq. 10} \quad \log k_2^{\text{rel}} = 1.207 \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) + 0.399\mu - 0.003 - 3$$

This result is surprising since these equations have only two variables. The reason why these two variable equations

TABLE V
Computed Rate Constants

SOLVENT	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	log k ₂ rel. ±3
BENZFL	0.932	2.295	0.888	0.948	0.857	0.868	0.877	0.858	0.854	0.923	0.78 Fluorobenzene
BENZCL	1.015	2.359	0.910	0.964	0.965	0.892	0.909	0.929	0.992	0.995	0.96 Chlorobenzene
BENZBR	1.089	2.395	0.960	0.993	1.063	0.926	0.981	1.021	1.008	1.083	1.00 Bromobenzene
BENZIO	0.916	2.207	0.690	0.716	0.918	0.706	0.705	0.787	1.019	0.943	1.10 Iodobenzene
TRANSE	0.249	1.556	0.219	0.283	0.273	0.320	0.199	0.125	0.197	0.325	0.38 trans-Dichloroethylene
CISDIC	1.038	2.200	1.174	1.242	1.240	1.141	1.311	1.224	1.027	1.081	1.16 cis-Dichloroethylene
DICL12	1.200	2.430	1.343	1.372	1.331	1.246	1.414	1.334	1.056	1.147	1.62 1,2-Dichloroethane
TETRAC	0.400	1.887	0.160	0.190	0.168	0.226	0.015	0.035	0.363	0.363	0.00 Tetrachloroethylene
TRICEA	1.095	2.534	1.036	1.124	0.956	1.000	1.012	1.002	1.204	1.032	0.60 Trichloroethane
TRICEE	0.680	2.005	0.597	0.653	0.613	0.628	0.589	0.561	0.624	0.705	0.66 Trichloroethylene
TETRAA	1.241	2.690	1.168	1.207	1.146	1.087	1.094	1.115	1.073	1.096	1.20 Tetrachloroethane
ODICLB	1.416	2.827	1.195	1.254	1.308	1.136	1.226	1.291	1.215	1.290	1.18 o-Dichlorobenzene
MDICLB	1.094	2.816	0.500	0.600	0.743	0.544	0.518	0.694	0.956	0.976	1.13 m-Dichlorobenzene
PDICLB	0.585	2.239	0.773	0.854	0.805	0.784	0.304	0.357	0.943	0.375	0.76 p-Dichlorobenzene
1D1CL	1.359	2.981	1.248	1.348	1.053	1.178	1.203	1.127	0.831	1.025	1.32 1,1-Dichloroethane
HEPTAN	0.604	2.830	0.155	0.084	0.227	0.011	0.334	0.217	0.009	0.285	-0.52 Heptane
CYHEXA	0.426	2.138	0.086	0.145	0.046	0.148	0.113	0.088	0.112	0.313	-0.38 Cyclohexane
CYHEXE	0.500	2.081	0.275	0.302	0.160	0.298	0.105	0.112	0.226	0.436	-0.12 Cyclohexene
CARTET	0.334	1.859	0.088	0.126	0.024	0.157	0.055	0.047	0.260	0.334	0.08 Carbontetrachloride
NBUETH	1.221	3.513	0.484	0.725	0.468	0.545	0.335	0.490	0.411	0.790	0.15 n-Butylether
PCYMEN	0.669	2.828	0.024	0.151	0.165	0.111	0.288	0.090	0.306	0.351	0.37 p-Cymene
PXYLEN	0.496	2.248	0.019	0.083	0.044	0.102	0.167	0.073	0.335	0.355	0.44 p-Xylene
CUMENE	0.702	2.621	0.055	0.183	0.172	0.163	0.074	0.075	0.368	0.501	0.48 Cumene
TOLUEN	0.533	2.043	0.246	0.321	0.275	0.329	0.166	0.198	0.375	0.511	0.55 Toluene
BENZEN	0.249	1.566	0.129	0.153	0.159	0.208	0.059	0.039	0.345	0.359	0.62 Benzene
DIOXAN	0.695	2.232	0.745	0.747	0.603	0.696	0.544	0.480	0.182	0.489	0.66 Dioxane
CLFORM	0.753	1.909	0.886	0.910	0.992	0.868	0.992	0.881	0.796	0.785	0.95 Chloroform
DICLME	0.889	2.009	1.058	1.113	1.223	1.042	1.248	1.121	0.981	0.929	1.14 Dichloromethane
NITRME	1.866	3.042	2.237	2.262	2.517	2.030	2.699	2.500	1.142	1.547	1.52 Nitromethane
NITRBE	2.193	3.448	2.175	2.218	2.255	1.971	2.334	2.351	1.426	1.981	1.63 Nitrobenzene
STYREN	0.448	1.977	0.048	0.107	0.179	0.155	0.042	0.041	0.476	0.435	0.82 Styrene
Avg. Dev.	0.39	1.85	0.35	0.36	0.33	0.32	0.40	0.39	0.23	0.22	Average Deviation

are the best is probably because they include only parameters which are important in determining the rates. If other parameters are included they either are not important or they are important only because they are related to parameters which have already been included. The next best equation, Eq. 6 with three variables, has an average deviation of 0.32.

The A, B, ... of the equations of Table II are related to certain theoretical quantities as follows.

If $\log k$ is a function of the physical properties of the solvent it is possible to write the total differential giving the change in $\log k$ with respect to changes in the solvent parameters P.

$$\log k = f(P_1, P_2, \dots, P_n)$$

$$d \log k = \sum_{i=1}^n \left(\frac{\partial f}{\partial P_i} \right) dP_i$$

In order to eliminate the differentials, $d \log k$ and dP_i , a standard is chosen and the differentials set equal to differences between the quantities for the solvent and for the standard.

$$d \log k = \log k - \log k_{\text{std}}$$

$$dP_i = P_i - P_{i\text{std}}$$

$$\log k - \log k_{\text{std}} = \sum_{i=1}^n \left(\frac{\partial f}{\partial P_i} \right) (P_i - P_{i\text{std}})$$

By taking all the rate constants relative to the rate constant of the standard $\log k_{\text{std}}^{\text{rel}}$ is made zero.

$$\log k^{\text{rel}} = \sum_{i=1}^n \left(\frac{\partial f}{\partial p_i} \right) p_i + \text{constant}$$

$$\text{constant} = \log k_{\text{std}}^{\text{rel}} - \sum_{i=1}^n \left(\frac{\partial f}{\partial p_i} \right) p_{i \text{ std}}$$

The partial differential quantities, $\left(\frac{\partial f}{\partial p_i} \right)$, were determined using multiple regression analysis carried out on an IBM 7040 computer and are the same as the A, B, ... mentioned above.

In order to further test the usefulness of the equations an attempt was made to predict the rate constants for another reaction. Assuming that the solvent effects in the two reactions will be proportional, the changes in the free energies of activation upon changing solvents can be made proportional.

$$\Delta \Delta F_1^\ddagger = c \Delta \Delta F_2^\ddagger \quad (1)$$

Then, assuming that k is correctly represented by the Eyring equation, the constant c can be found as follows:

$$\begin{aligned} k_1^A &= A \exp(-\Delta F_A/RT) \\ k_1^B &= A \exp(-\Delta F_B/RT) \end{aligned} \quad (2)$$

$$RT \log \frac{k_1^A}{k_1^B} = -\Delta \Delta F_1^\ddagger$$

and similarly for reaction 2 in the two solvents A and B,

$$RT \log \frac{k_2^A}{k_2^B} = -\Delta \Delta F_2^\ddagger \quad (3)$$

then c can be found from Equation 4 using the known values.

$$c = \frac{\log k_1^A - \log k_1^B}{\log k_2^A - \log k_2^B} \quad (4)$$

Instead of using only two solvents as above as many as possible should be used and c determined from the slope of a plot of $\log k_1$ values versus $\log k_2$ values.

The slope was found using values for the reaction of triethylamine with ethyl iodide in six solvents, listed in the first part of Table VI, by the method of least squares. The rate constants for the Menschutkin reaction are those of Ruf, Grimm, and Wolff¹⁸. c turns out to be approximately 1.1 and the predicted values for the rate constants along with measured rate constants and the average deviation are listed in Table VI. The values are predicted by taking the rate constants for TBF decomposition calculated by Equation 10 and using the following equation, which follows from (4). The average deviation of the values calculated

$$\log k_1^A = c \log k_2^A + (\log k_1^B - c \log k_2^B)$$

in this way from the experimental values is 0.31 for 8 solvents.

This work has accomplished two things; first, the TBF rate constant empirical solvent polarity scale has been extended and second, equations which can be used to predict the rate of a polar reaction have been found.

There are now available rate constants for ionic TBF

TABLE VI

Calculated Rate Constants for the
Menschutkin Reaction

Solvent	$\log k_{\text{obs}}^{\text{TBF}}$	$\log k_{\text{calc}}^{\text{TBF}}$	$\log k_{\text{calc}}^{\text{M}}$	$\log k_{\text{obs}}^{\text{M}}$
Fluorobenzene	-1.52			-3.04
Chlorobenzene	-1.32			-2.86
Bromobenzene	-1.30			-2.80
Iodobenzene	-1.20			-2.57
<u>o</u> -Dichlorobenzene	-1.12			-2.60
<u>p</u> -Dichlorobenzene	-1.54			-2.95
Cyclohexane	-2.68	-2.62	-4.26	-5.00
Toluene	-1.75	-1.79	-3.36	-3.60
Benzene	-1.68	-1.94	-3.52	-3.40
Nitrobenzene	-0.62	-0.32	-1.72	-1.86
<u>p</u> -Xylene	-1.86	-1.94	-3.54	-4.10
<u>m</u> -Dichlorobenzene	-1.17	-1.32	-2.83	-3.16
Phenetole		-1.54	-3.08	-2.93
Benzonitrile		-0.31	-1.72	-1.95
Average Deviation				0.31

decomposition in 34 non-hydroxylic solvents. I believe these rate constants should provide a better means of correlating rate data for polar reactions than systems based on solvatochromism, simply because the substrates are more similar.

The equations allow the system to be extended to hydroxylic solvents and in fact to any solvent whatsoever. Nevertheless, this treatment is only empirical and will hopefully be made unnecessary along with the others when the theory of the liquid state has advanced sufficiently.

EXPERIMENTAL

A. Synthesis of t-Butylperoxyformate

Two different methods were used, one by Pincock⁹ and one by Ruchardt²¹. The method of Pincock involves first making formic acetic anhydride which is then reacted with t-butylhydroperoxide. Ruchardt's preparation involves just the reaction of formic acid with t-butylhydroperoxide.

1) t-Butylhydroperoxide

Lucidol t-butylhydroperoxide (500 ml) was distilled under vacuum in an azeotrope distillation apparatus until the distillate no longer separated into two phases. Three fractions were then collected after discarding the material which distilled below 39° at 22 mm. The first fraction of about 50 ml boiled at 39°-40° at 22 mm, the second of about 100 ml at 40° at 22 mm and the third of about 100 ml at 40-41° at 22 mm.

2) Formic acetic anhydride⁹

Commercial formic acid, 100 ml of 98%, was treated with a stream of ketene gas passed through a trap held at 0° for four hours. The ketene was generated by passing acetone over red-hot wires. The reaction mixture was then distilled under vacuum and three fractions collected; the first, 70 g., boiling at 25-34° from 80 to 20 mm, the second boiling at 34-38° at 20 mm, 67.7 g and a small third fraction boiling

at 38-40°C at 20 mm.

3) t-Butylperoxyformate⁹

To 30 g of formic acetic anhydride in 100 ml of light pet. ether was added a solution of 20 g t-butylhydroperoxide over about one hour at 0° with vigorous stirring. The reaction mixture was held at 0° with stirring for 18 hours. After 18 hours the mixture had only one phase; it was then washed with 150 ml of water in 10 ml portions, dried over anhydrous magnesium sulfate and the solvent evaporated. The remaining liquid was distilled under vacuum using shields and keeping the pot temperature below 55°. Three fractions were collected all of which had good infrared spectra compared to an authentic spectrum. The first fraction, 4.6 g, was collected at 23-36° at 20 mm; the second from 36° at 20 mm to 30° at 10 mm; and the third at 34° at 20 mm..

4) t-Butylperoxyformate²¹

t-butylhydroperoxide, 30 g, and 30 g 98% commercial formic acid in 200 ml lt. pet. ether were stirred at 50° overnight in an apparatus for continuous extraction of water. After 24 hours there was only one phase, which was then washed about 30 times with water, dried over anhydrous magnesium sulfate and the solvent evaporated. The remaining liquid was distilled under vacuum and two fractions, both having good infrared spectra, were collected. Both

boiled at 41° at 22 mm, each was about 5 ml.

B. Pyridine and Quinone

Pyridine was used as the base in all the runs.

Eastman White Label grade was distilled from barium oxide and sodium hydroxide at atmospheric pressure, b.p. 115° .

Quinone, used as a radical inhibitor, was purified by sublimation.

C. Purification of Solvents

1) Fluorobenzene

Eastman White Label grade was used without further purification.

2) Chlorobenzene

Eastman White Label grade was washed with concentrated sulfuric acid, then with water and dried over calcium chloride. The solvent was then distilled through a two foot Vigreux column, b.p. 132° .

3) Bromobenzene

Practical grade material was distilled first from phosphorous pentoxide then from anhydrous potassium carbonate, b.p. $155-156^{\circ}$.

4) Iodobenzene

Eastman White Label grade was washed with aqueous sodium thiosulfate, dried over calcium chloride and then over phosphorous pentoxide, and finally distilled under vacuum, b.p. 50° at 4 mm.

5) trans-Dichloroethylene

Eastman Practical grade was distilled at atmospheric pressure, b.p. 48° . Gas-liquid chromatography showed that this trans isomer contained about 8% cis isomer.

6) cis-Dichloroethylene

Eastman White Label grade was distilled at atmospheric pressure, b.p. 60° . Gas-liquid chromatography showed that this solvent contained about 3% trans isomer.

7) 1,2-Dichloroethane

Eastman Spectrograde material was used without further purification.

8) Tetrachloroethylene

Eastman Spectrograde material was used without further purification.

9) 1,1,1-Trichloroethylene

Eastman Technical grade was shaken with concentrated hydrochloric acid, then with 10% potassium carbonate solution and finally with saturated sodium chloride solution. The solvent was then dried over anhydrous magnesium sulfate and distilled, b.p. $74-75^{\circ}$.

10) Trichloroethylene

Eastman White Label grade was distilled at atmospheric pressure and the fraction boiling at 85.7° at 751 mm collected.

11) o-Dichlorobenzene

Eastman White Label grade was distilled at atmospheric

pressure, b.p. 180° .

12) m-Dichlorobenzene

Practical grade was washed with 10% sodium hydroxide and then with water until the washings were no longer basic. The solvent was then dried over anhydrous magnesium sulfate and distilled at atmospheric pressure, b.p. 173° .

13) p-Dichlorobenzene

Chemically pure material was used without further purification, m.p. 55° .

14) Tetrachloroethane

Eastman White Label grade was washed with concentrated sulfuric acid once, then with water until the washings were no longer acidic. The solvent was then dried over anhydrous magnesium sulfate and distilled at atmospheric pressure, b.p. 146° .

D. Kinetic Procedure

The method was similar to that of Pincock⁹. A small amount of a mixture of TBF and pyridine in the solvent under study was made up and specially prepared test tubes having a constriction were filled with one to two mls of the mixture. The tubes were then sealed and lowered into the oil bath in a special sample holder. The samples were withdrawn after varying times and quenched in an ice bath.

Since p-dichlorobenzene is a solid at room temperature a special technique was necessary. A weighed amount of

pyridine was dissolved in a known amount of solvent and this mixture was held at 90° in a small flask. After adding an appropriate amount of TBF, 1 ml aliquots were withdrawn with pipettes previously heated to 110° and discharged into 2 ml portions of benzene. These p-dichlorobenzene-benzene mixtures were then analyzed in the usual manner.

Analysis of the samples was carried out by measurement of the loss of carbonyl absorption at 1760 cm⁻¹ on an Infra-red spectrophotometer. Before making any measurements of samples the machine was set to read zero absorbance with pure solvent in both beams and infinity with the sample beam completely blocked. The relative concentration at time t was calculated by the equation,

$$\frac{P_0}{P} = \frac{A_\infty - A_0}{A_\infty - A}$$

Plots of $\log \frac{P_0}{P}$ versus time were straight lines and the decomposition was usually followed to about 75%. Second order rate constants were obtained by dividing the slope by the concentration of pyridine used in the run and multiplying by 2.303.

The best straight line was fitted visually to the points with due note taken that a constant error in the extent of reaction, A, becomes an increasing error in $\log (A_\infty - A)$.

Streitwieser, Van Sickle and Langworthy²² state, "A careful analysis shows that this procedure is clearly superior to the usual least squares method."

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APPENDIX

A. Regression Analysis

The log of the rate constant y_j in a solvent j can be expressed as a linear combination of regression coefficients, b_i , and solvent parameters, x_{ij} , plus an error, ϵ_j .

$$y_j = \sum_i b_i x_{ij} + \epsilon_j$$

$$\epsilon_j^2 = (y_j - \sum_i b_i x_{ij})^2$$

$$\sum_j \epsilon_j^2 = \sum_j (y_j - \sum_i b_i x_{ij})^2$$

In order to minimize the error, the derivative of with respect to the regression coefficients is set to zero.

$$\frac{\partial \sum \epsilon_j^2}{\partial b_i} = 2 \sum_j x_{ij} (y_j - \sum_i b_i x_{ij}) = 0$$

$$= \sum_j x_{ij} y_j - \sum_j b_i \sum_i x_{ij}^2$$

or

$$\sum_j x_{ij} y_j = \sum_j b_i \sum_i x_{ij}^2$$

The last equation yields a set of linear equations in b_i which can be solved for the regression coefficients which minimize the error.

A statistical quantity called the "F ratio" and defined as $\left(\frac{b_i}{\Delta b_i}\right)^2$ was also computed. If the F ratio of a regression coefficient is less than unity then the variable

associated with that coefficient is not related, according to this method of calculation, to the log k. Little use of F ratios was made in choosing variables.

B. Computing

A program from the University of British Columbia Computing Center library was used to calculate the regression coefficients and F ratios. A program was written for computing the $\log k^{\text{rel}}$ presented in Table V. All computing was done on an IBM 7040 computer.