The alkali extracts were combined, cooled in an ice bath, and acidified with cold, dilute hydrochloric acid. The phenolic product was taken up in ether, the solution was dried, and the ether was removed *in vacuo*. The residue was weighed and analyzed for *cis* and *trans* isomer by the infrared method. The concentration of *trans* phenol was effectively invariant as the reactions proceeded, as is shown in typical runs (see Table I).

Analysis. All analyses were carried out on a Perkin-Elmer Model 21 infrared spectrometer using a single fixed cell with sodium chloride windows and having a 0.05-mm. path length. Total phenol concentration was determined using the band at 3460 cm.$^{-1}$ in carbon disulfide solutions have concentrations lying in the range of 10–15%. The bands at 965–970 and 705–715 cm.$^{-1}$ were used to determine the *trans* and *cis* double bond contents, respectively. Samples of the pure isomeric ethers and phenols in known concentrations were used to establish standard curves for the relation between absorbance and concentration, and these were used to ascertain concentrations of the unknown solutions.

N.m.r. Spectra. The n.m.r. spectra were determined using a Varian A-60 spectrometer,[45] in carbon tetrachloride solutions using tetramethylsilane as an internal standard.

Effects of Nonpolar Solvents on an Ionic Reaction. II. Catalyst Basicity, Activation Parameters, Salt Effects, and Deuterium Isotope Effects in the Ionic Decomposition of *t*-Butylperoxy Formate

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Formate C–H bond breakage in the initial step for base-catalyzed decomposition of t-butylperoxy formate to carbon dioxide and t-butyl alcohol in nonhydroxylic solvents is established by kinetic deuterium isotope effect ratios (k_H/k_D = 4.1 for the pyridine-catalyzed reaction in heptane or chlorobenzene at 90°). For a wide variety of bases, the Brønsted relation (with log k_2 = 0.64pK$_a$ − 5.35) is followed in chlorobenzene with no steric effect observed for ortho-substituted bases. Triethylamine is 660 to 1380 times more effective as a catalyst than pyridine but the pattern of solvent effects remains the same (heptane << benzene < chlorobenzene < nitrobenzene). Changes in media by addition of salts to polar solvents (LiClO$_4$ to acetonitrile) or polar compounds to nonpolar solvents (pyridine to heptane) cause small increases in rates. The rates in heptane–benzene mixtures and the lower activation energies and more negative activation entropies found in benzene are consistent with the expected effect of polarization of solvent. Solvent effects in some other dipolar reactions in nonhydroxylic solvents are similar to those found in ionic decomposition of t-butylperoxy formate, but no general relationship is found.

t-Butylperoxy formate (I) (TBF), a peroxide highly stable toward thermal free radical decomposition, readily decomposes to carbon dioxide and *t*-butyl alcohol when catalyzed by bases.[1] The kinetic acceleration of this catalyzed decomposition when the solvent is made more ionic or more polarizable indicates formation of a polar transition state. Rate and prod-

uct comparisons[1] suggest that attack by base occurs directly on the formate hydrogen with concerted formation of carbon dioxide in the rate-determining step.
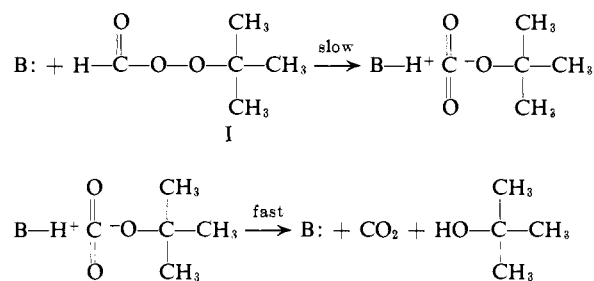
In this mechanism the formation of a dipolar transition state, with separation of the charged centers by the CO$_2$ unit, is made possible even in nonpolar, weakly polarizable solvents by concurrent partial formation of the stable carbon dioxide molecule.

To establish definitely that this reaction involves hydrogen transfer in the slow step, the deuterium isotope effect for ionic reaction of *t*-butylperoxy formate-*d* has been investigated. In addition, the possibility that the dipole moment of the transition state might be varied by changes in the basic strength of the catalyst or by a change in solvent has been investigated. Further aspects of solvation for this ionic elimination reaction in nonpolar, nonhydroxylic solvents are also reported here. These include studies of salt effects, rates in mixed solvents, and measurements of activation parameters.

(1) R. E. Pincock, *J. Am. Chem. Soc.*, **86**, 1820 (1964).

Results and Discussion

t-Butylperoxy Formate-d. Reaction of formic-*d* acid with ketene to yield formic-*d* acetic anhydride and subsequent reaction of this with *t*-butyl hydroperoxide gave *t*-butylperoxy formate-*d*. (TBF-*d*). Although TBF possesses an ordinary single carbonyl absorption at 1760 cm.$^{-1}$, TBF-*d* shows two bands of near equal intensity at 1693 and 1735 cm.$^{-1}$. The relative intensity of these two bands was not changed by subjecting the samples to further purification procedures nor by dilution in various solvents. Neither were the bands accounted for by impurities such as formic acid or formate esters. Direct proof that the two carbonyl bands originated from TBF-*d* itself was obtained by measuring the decrease in intensity of each band during decomposition of the peroxide in dilute solutions. The rate of loss of both bands under several different conditions (see Table I) was the same, so a single species is responsible for both absorption bands. This appar-

Table I. Isotope Effects in the Base-Catalyzed
Decomposition of *t*-Butylperoxy Formate at 90°

Solvent	Base	k_D, moles l.$^{-1}$ sec.$^{-1}$	k_H, moles l.$^{-1}$ sec.$^{-1}$
Chloroben-zene	Pyridine	$1.09 \pm 0.05^{b,d}$ $\times 10^{-2}$	4.50 ± 0.04^{b} $\times 10^{-2}$
		$k_H/k_D = 4.13 \pm 0.23^{c}$	
Chloroben-zene	Et$_3$N	12.9 ± 1.1^{d}	42.2 ± 3.3
		$k_H/k_D = 3.27 \pm 0.54$	
Heptane^{a}	Pyridine	0.0409 ± 0.001^{d} $\times 10^{-2}$	0.166 ± 0.012 $\times 10^{-2}$
		$k_H/k_D = 4.06 \pm 0.39$	
Heptane	Et$_3$N	0.687 ± 0.007	2.32 ± 0.16
		$k_H/k_D = 3.38 \pm 0.27$	

^{a} The rate in this solvent is sensitive to high pyridine concentration; all these rate measurements at 0.101 M pyridine. ^{b} Average deviation in rate constant in two or three runs. ^{c} Maximum deviation in rate ratio based on average deviation of rate constants. ^{d} Runs carried out by measurement of loss of either the 1693- or 1735-cm.$^{-1}$ band of TBF-*d* agreed within the deviations listed.

ently unique doubling of carbonyl absorption on isotopic substitution of adjacent hydrogen appears to be a simple example of Fermi resonance interaction.[2] The vibrational spectra of formic acid and formic-*d* acid have been completely analyzed and interpreted[3]; comparison of shifts in absorption bands in formic acid and formic-*d* acid with those of TBF and TBF-*d* points out the origin of the interaction. The carbon–hydrogen out-of-plane bending vibration (1033 cm.$^{-1}$) in formic acid[3] is shifted to 837 cm.$^{-1}$ in formic-*d* acid (a ratio of 1.23), a band appearing at 1070 cm.$^{-1}$ in TBF is absent in TBF-*d*, and a new, but weak, band appears at 860 cm.$^{-1}$ (ratio of 1.24). The first overtone of this absorption would fall at 1720 cm.$^{-1}$ and possess the symmetry required to interact with the carbonyl absorption in this region.[4] The result is a resonance interaction yielding the two observed absorption bands.[5] Yates

and Williams[6] have described and similarily interpreted an inversely related case in which certain 2-cyclopentenones loose double carbonyl absorption when deuterium is substituted for hydrogen at the 2-position.

Kinetic Isotope Effects. The kinetic isotope ratios, k_H/k_D, in chlorobenzene and in heptane were obtained by separate direct rate measurements on TBF and TBF-*d* (greater than 99% deuterated at formate hydrogen). The large k_H/k_D ratios obtained (Table I) establish formate C–H bond breakage in the rate-determining step and support the mechanism given above.

Although the magnitude of a hydrogen isotope effect is not a direct measure of the extent of bond breakage,[7] the isotope effects observed here are near the maximum 4.9 calculated for loss of one C–H stretching vibration[8] at 90° and are consistent with considerable bond breakage in development of the dipolar transition state. Within the maximum deviation, the isotope effects in chlorobenzene and heptane are the same when the same basic catalyst is used. Although the rates vary by a factor of 25 between these solvents, the extent of bond breakage as indicated by the isotope effects is not noticeably different in the two solvents. Apparently the transition state for decomposition in either solvent has the same extent of bond breakage (internal structure). The greater rate in chlorobenzene compared with that in heptane is brought about only by more effective solvation (external structure) of the transition state. Frisone and Thornton[9] have evidence from isotope effects that in the solvolysis of *t*-butyl chloride in hydroxylic solvents the extent of bond breakage at the transition state is determined by the substrate bonds involved and not by the nature of the solvent present. The solvolysis of *t*-butyl chloride and the base-catalyzed decomposition of TBF are similar in that ionic transition states are formed from relatively nonpolar reactants. In theoretical treatments of solvent effects on dipolar reactions[10] the assumption of an invariant dipole moment for the transition state in solvents with differing solvation properties is commonly made. This simplifying assumption is then experimentally supported for these two ionic reactions.

Effect of Base Strength. The catalytic efficiency of various nitrogen bases was investigated in chlorobenzene at 90°. These results are illustrated in Figure 1 where log k_2 is plotted against the pK_a(water) of the conjugate acid of the base.[11] A great range of reactivity is found, k_2 varying over seven powers of ten while base strength varies by ten pK_a units from weakly basic *o*-nitroaniline up to triethylamine. The Brønsted relation (log $k_2 = 0.64$p$K_a - 5.35$) is followed; the strongest base is the most efficient catalyst. The tertiary amines are slightly more effective catalysts than

turbed component vibrations. The unperturbed carbonyl absorption in TBF-*d* apparently would be between the observed 1693- and 1735-cm.$^{-1}$ bands, shifted by isotopic mass effects from the 1760 cm.$^{-1}$ observed in normal TBF.

(2) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1954, p. 215.

(3) L. M. Sverdlov, *Dokl. Akad. Nauk, SSSR*, 91, 503 (1953).

(4) See ref. 2, pp. 101, 124, 216.

(5) This vibrational resonance interaction gives rise to bands of greater and lesser energies relative to the average energy of the unper-

(6) P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, 80, 5896 (1958).

(7) R. F. W. Bader, *Can. J. Chem.*, 42, 1822 (1964); F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

(8) K. B. Wiberg, *ibid.*, 55, 713 (1955).

(9) G. J. Frisone and E. R. Thornton, *J. Am. Chem. Soc.*, 86, 1900 (1964).

(10) See K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 379

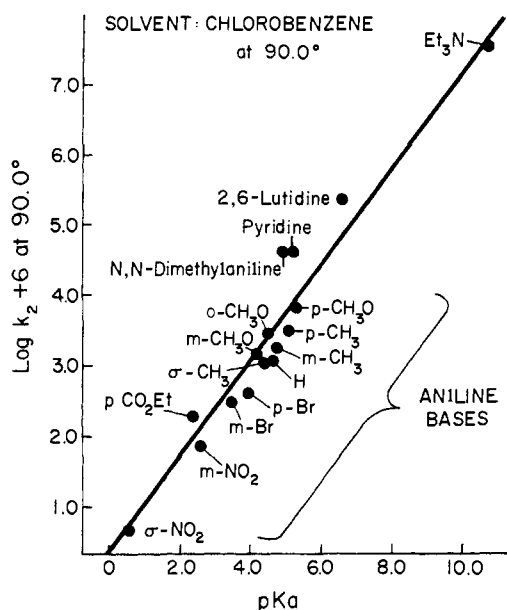(11) pK_a values from M. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, 52, 5115 (1930); 54, 3469 (1932).

Figure 1. Effect of base strength, in terms of pK_a of conjugate acids in water at 25°, on log k_2 for reaction of bases with t-butyl-peroxy formate in chlorobenzene at 90°.
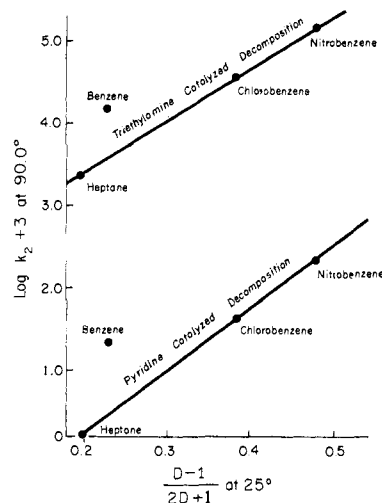

Figure 2. Log of second-order rate constant for pyridine- and triethylamine-catalyzed decomposition of t-butylperoxy formate against a function of dielectric constant of solvent.

the primary aniline bases (relative to their respective pK_a values) but a good linear relationship of log k_2 to pK_a holds even for sterically hindered bases. For example, 2,6-lutidine, a stronger base than pyridine, which, however, sometimes shows decreased catalytic efficiency relative to pyridine,[12] gives a greater rate of reaction with TBF than does pyridine. 2,6-Dimethyl-aniline gives the same rate as aniline, and several other ortho-substituted anilines are still relatively effective catalysts. Such results are indicative of reaction of base with formate hydrogen (with little steric hindrance) rather than nucleophilic attack on other atoms of TBF such as the peroxide oxygens. When proton transfer is involved, steric effects are commonly negligible except for very highly hindered bases.[12]

As a relative measure of response to substituent effects and as a rough measure of charge development in the base-catalyzed decomposition of TBF, the ρ-value of -1.9 for reaction of meta- and para-substituted anilines in chlorobenzene at 90° may be compared with that of about -4 calculated from data of Bell and Bayles[13] for protonation (with ion pair formation) of a few substituted anilines by a standard base in chlorobenzene at 25°. At a temperature of 25° the corrected ρ-value for reaction of TBF would be more negative than -1.9.[14] This large negative ρ-value suggests considerable build-up of positive charge on the basic catalyst in TBF decomposition.

Since the formation of a polar transition state in the TBF–base reaction is well established by solvent, isotope, and substituent effects, it is of interest to see if the polarity of the transition state may be varied by a change in catalyst. The change in rate with solvent for a reaction which forms a dipolar transition state from

(12) F. Coviiz and F. H. Westheimer, J. Am. Chem. Soc., 85, 1773 (1963); J. A. Feather and V. Gold, Proc. Chem. Soc., 306 (1963); E. S. Lewis and J. D. Allen, J. Am. Chem. Soc., 86, 2022 (1964).
(13) R. P. Bell and J. W. Bayles, J. Chem. Soc., 1518 (1952).
(14) Rates for triethylamine- and pyridine-catalyzed reaction of TBF at 90° and at 70° show the reaction is more sensitive to catalyst basicity at lower temperatures.

relatively nonpolar reactants varies with the dipole moment of the transition state.[10] Changes of the transition state dipole moment might be a cause of rate differences when the catalysts have different electron donating abilities. However, the dipolar properties of the two reactions involving TBF decomposition catalyzed by triethylamine and by pyridine, which differ widely in base strength, are very similar. This is shown in Figure 2, where rates in heptane, benzene, chlorobenzene, and nitrobenzene for triethylamine and pyridine-catalyzed decomposition are plotted against a theoretical, if oversimplified,[1] measure of solvation property of the media.[10] The same pattern of solvent effects is found with both catalysts although the rates are widely different. The slopes of the lines shown, which are a measure of the relative dipole moment change in the reactions, are nearly the same. Essentially the same extent of dipole moment development, independent of the base catalyst, must be attained in the transition state for ionic decomposition of TBF. A more basic catalyst just allows this required state to be more easily reached and the rate is correspondingly faster. This result complements the result from isotope effects: the dipole developed at the transition state is not sensitive to properties of the solvent nor greatly dependent on the catalyst used. Thus the base-catalyzed decomposition of TBF does not show the "spectrum" of different mechanisms commonly found in other elimination reactions when different bases and solvents are used.[15] The ionic reaction of TBF is a comparatively simple reaction; to complete the reaction a certain amount of bond breakage with dipole formation is required at the transition state, the means of reaching this state depending to varying extents on the solvation possible in a given medium.

Polarizability and Rates in Heptane–Benzene Mixtures. Two properties of a solvent which contribute to its ability to aid the separation of charge in a dipolar reaction are dipole moment and polarizability. The orientation of permanent solvent dipoles by the dipole

(15) W. H. Saunders, Jr., and D. H. Edison, J. Am. Chem. Soc., 82, 138 (1960); R. G. Pearson and D. C. Vogelsong, ibid., 80, 1048 (1958); H. Kwart, T. Takeshita, and J. L. Nyce, ibid., 86, 2606 (1964).
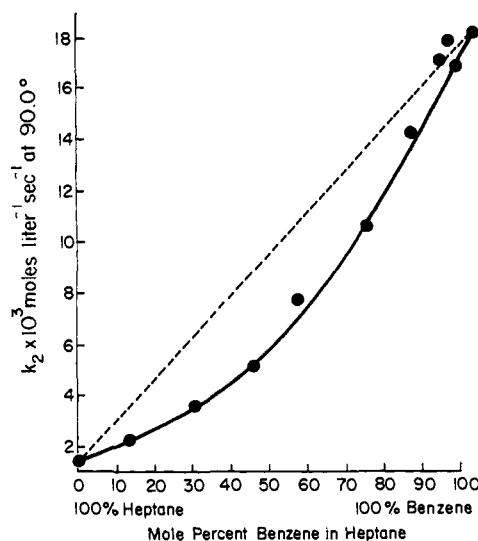
Figure 3. Relation of second-order rate constants for reaction of 0.03 M t-butylperoxy formate with 0.05 M pyridine to the composition of benzene–heptane solvent mixtures.

Figure 4. Salt effects on the second-order rate constant for reaction of t-butylperoxy formate with pyridine in acetonitrile at 50°.

developed in the ionic reaction of TBF is important in solvents of high dielectric constant, while induced polarization of the solvent is important in solvents of low dielectric constant.[1]

Two solvents which have no permanent dipoles but still bring about a rate difference of fourteen in the TBF–pyridine reaction are heptane and benzene. Figure 3 shows the rates of TBF decomposition, at constant pyridine concentration, in mixtures of benzene with heptane. If specific solvation of the dipolar transition state by only a few benzene molecules occurred, the rate in benzene should not be decreased rapidly on addition of heptane to benzene. However, as shown in Figure 3 the accelerative effect of benzene is rather effectively cut down by addition of heptane to pure benzene. The beneficial solvation occurring in benzene then appears to be due to the polarization of many benzene molecules in the vicinity of the transition state and the effectiveness of such solvation is broken up by the presence of a few heptane molecules. In a polarizable media of low dielectric constant such as benzene, the electric field of the dipolar transition state would be effective at relatively great distances in causing induced polarization of solvent molecules. Polarization of the medium as a factor in aiding dipolar decomposition of TBF–pyridine is also supported in that a plot of refractive index (a measure of polarizability)[1] of benzene–heptane mixtures against mole per cent gives a curved line similar to that of Figure 3.

Salt Effects and the Effects of a Polar Substance in Nonpolar Media. Figure 4 shows the effect of added salts on the rate constant for TBF reaction with pyridine in acetonitrile at 50°. Small positive salt effects are observed for LiClO₄ and NaClO₄, while there is no effect of tetra-n-butylammonium perchlorate. As expected, silver perchlorate causes a decrease in rate due to reaction with pyridine. Although the order Li > Na > n-Butyl₄N is the same observed[16] for salt effects on the ionization of p-methoxyneophyl p-toluenesulfonate in nonpolar solvents, the effects observed here

(16) S. Winstein, E. C. Friedrich, and S. Smith, *J. Am. Chem. Soc.*, **86**, 305 (1964); S. Winstein, S. Smith, and D. Darwish, *ibid.*, **81**, 5511 (1959).
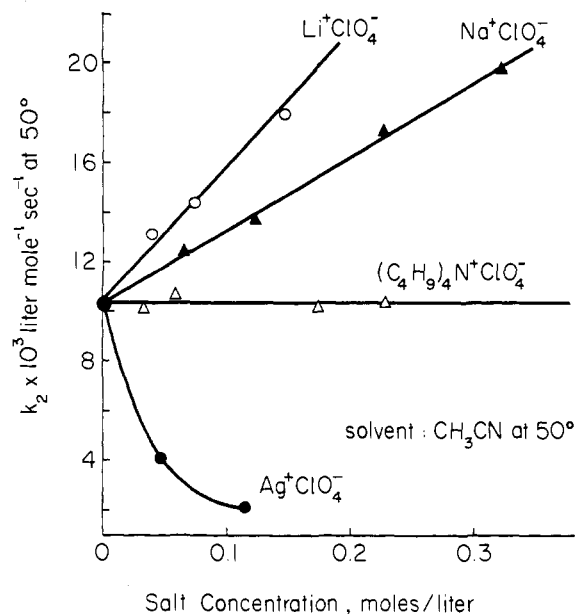
are much smaller. In dimethoxyethane, 0.3 M lithium perchlorate causes only a 3.5-fold increase in TBF–pyridine rate compared to 10^5 observed for 0.1 M lithium perchlorate in the tosylate reaction in ether. Rather than a specific electrophilic salt effect,[16] the less dramatic effect of lithium perchlorate on ionic TBF decomposition seems to be due to a macroscopic medium effect. In acetonitrile and dimethoxyethane highly polar salt ion pairs aid formation of the dipolar TBF–pyridine transition state. Other polar materials in a relatively nonpolar solvent also show accelerative abilities. Thus the presence of pyridine greater than 0.1 M increases the second-order rate constant for reaction with TBF in heptane so that at 0.7 M pyridine the rate is two and a half times greater than with 0.01 M pyridine (see Table II). These accelerative effects

Table II. Rates of Decomposition of t-Butylperoxy Formate Catalyzed by Pyridine in Heptane at 90.0°

Peroxide concn., M	Pyridine concn., M	$k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
0.0291	0.0105	1.45
0.0259	0.0265	1.70
0.0291	0.0495	1.42
0.0243	0.106	1.65
0.0237	0.232	2.01
0.0261	0.307	2.12
0.0253	0.356	2.60
0.0237	0.396	2.88
0.0260	0.521	2.92
0.0260	0.612	3.44
0.0253	0.730	3.93

of salt ion pairs and of the polar compound pyridine are similar to the weakly accelerative effects of salts or polar compounds in the dipolar reaction of methyl bromide with pyridine in benzene.[17] The close similarity in solvent effects between the dipolar TBF–base

(17) Y. Pocker, *J. Chem. Soc.*, 1279 (1957).

and the ionic alkyl halide–base reactions has been pointed out.[1]

Activation Parameters. The enthalpy and entropy of activation for both pyridine- and triethylamine-catalyzed reaction of TBF in four solvents were calculated from rates measured at 70 and 90°. The values are gathered in Table III. As found in other dipolar reactions,[18] low values of activation energy are accompanied by large negative entropies of activation.[19] In the aromatic solvents the rates are dominated by the entropy term so that the solvent with the greatest activation energy is actually the "fastest." The greatest negative ΔS^* is found for benzene. As a consequence of the ionic nature of the reaction considerable orientation of solvent is required in nonpolar solvents to allow the heterolytic bond breakage and charge development to proceed. As benzene has no dipole moment it is not greatly ordered in the liquid state, but it is, relative to heptane, quite polarizable. Since its dielectric constant is also low many benzene molecules may be "frozen," even at great distances, by the dipole formed in TBF decomposition.

Table III. Activation Parameters for the Base-Catalyzed Decomposition of *t*-Butylperoxy Formate

Solvent	Relative rate at 90°	ΔH^*, kcal.	ΔS^*, e.u.
Pyridine-catalyzed decomposition			
Heptane	1.0	16.2	−27.
Benzene	13.0	14.1	−28.
Chlorobenzene	25.7	15.4	−23.
Nitrobenzene	133	19.4	−8.6
Triethylamine-catalyzed decomposition			
Heptane	1.38×10^3	10.9	−27.
Benzene	9.45×10^3	3.4	−44.
Chlorobenzene	22.3×10^3	6.4	−34.
Nitrobenzene	87.5×10^3	9.2	−24.

Pearson[20] has calculated from the experimental dielectric constant properties of various solvents the changes in activation parameters expected for a reaction having an invariant extent of charge development (as is indicated for the case of TBF decomposition). Benzene and heptane are placed in a group for which a less negative entropy of activation and a greater enthalpy of activation than chlorobenzene and other more polar solvents is predicted. The general failure[21] of the prediction for the case of benzene seems due to the importance of polarizability. This apparently is a more important factor in determining rates and activation parameters in a solvent than is predicted by consideration of its dielectric constant alone.

The values of ΔH^* and ΔS^* are linearly related (ΔH^* = $280\Delta S^*$) for both pyridine- and triethylamine-catalyzed decomposition in benzene, chlorobenzene, and nitrobenzene. For both catalysts the point for heptane lies far off the line given by the aromatic solvents. Application of a suggested criterion[22] for the reality

of such isokinetic relationships[23a] (assuming an error of 10% in TBF rate constant measurements) gives a change in ΔH^* due to experimental error of 4.9 kcal., while the observed range is only 5.8 kcal. However, the sequence of points along the line (benzene < chlorobenzene < nitrobenzene), with heptane above the line, for both catalysts is reasonable[23a] in terms of beneficial solvation (lower ΔH^*) with accompanying constraint in solvent freedom (lower ΔS^*) when the solvent has been oriented by the polar transition state.

Solvent Effects in Dipolar Reactions. The solvent effects for the reaction of TBF with pyridine in nonhydroxylic solvents are closely related to solvent effects in some other dipolar reactions.[1] A plot of log k_{TBF} against log $k_{reaction}$ shows a good linear relationship for the reaction of methyl iodide with pyridine,[23b] triethylamine with ethyl iodide,[24] the decomposition of α-methylallyl chloroformate,[25] and the mutarotation of 5α,6β-dibromocholestane.[26,27] Howard and Ingold[28] have pointed out the similarity of solvent effects in the TBF–pyridine reaction with those for the autoxidation of styrene. However, no relationship is found for other polar reactions[29] which show solvent effects in hydroxylic solvents that correlate with empirical measures of solvent "ionization power."[29–31] Even in the above-mentioned reactions certain solvents specifically bring about a rate increase in individual cases.[27] Although the general feature of relatively accelerated rates in more polarizable solvents (*e.g.*, aromatic solvents) is found, effects and conditions peculiar to the individual reactions (specific solvation, autocatalysis, catalysis by trace impurities, and high reagent concentrations) indicate the difficulty of comparing, in any general manner, solvent effects in nonhydroxylic, nonpolar solvents.

Experimental

Materials. Formic-*d* acid (minimum isotopic purity 99%) was obtained from Merck Sharp and Dohme of Canada. Pyridine and triethylamine were refluxed and distilled from barium oxide. Commercially available solid amines used as catalysts were recrystallized and dried under vacuum. Liquid amines were freshly distilled, usually from zinc dust, with collection of the center fraction. 2,6-Dimethylaniline (Eastman Organic Chemicals) was used directly. 2,6-Lutidine was refluxed with methyl *p*-toluenesulfonate,[32] then distilled and redistilled from barium oxide.

(18) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 137.

(19) These activation parameters contrast with the values for thermal first-order free radical decomposition of TBF in chlorobenzene: ΔH^* 38 kcal., ΔS^* 15 e.u.

(20) R. G. Pearson, *J. Chem. Phys.*, 20, 1478 (1952).

(21) See ref. 10, p. 387 and ref. 18, p. 142.

(22) R. C. Petersen, J. D. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, 83, 3819 (1961); R. C. Petersen, *J. Org. Chem.*, 29, 3133 (1964).

(23) (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 324; (b) N. J. T. Pickels and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936).

(24) H. G. Grimm, H. Ruf, and H. Wolff, *Z. physik. Chem.*, 13B 301 (1931).

(25) K. L. Olivier and W. G. Young, *J. Am. Chem. Soc.*, 81, 5811 (1959).

(26) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, 35, 782 (1952).

(27) Chloroform is a far more effective solvent than expected from the correlation given by four other solvents (heptane, CCl₄, benzene, and nitrobenzene).

(28) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 42, 1044 (1964).

(29) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, 83, 618 (1961).

(30) E. J. Kosower, *ibid.*, 80, 3251 (1958).

(31) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, 84, 277 (1962).

(32) J. A. Cathcart and D. D. Reynolds, *ibid.*, 73, 3504 (1951).

Reagent lithium perchlorate hydrate (G. Fredrich Smith Chemical Co., Columbus, Ohio) was dried at 80° (24 hr.), then at 140° (48 hr.) under vacuum. Silver perchlorate and sodium perchlorate were dried under vacuum at 100–140° over phosphorus pentoxide. Tetra-n-butylammonium perchlorate was prepared from tetra-n-butylammonium iodide (Eastman Organic Chemicals) by treatment with silver perchlorate in ethanol. After recrystallization from 3:1 water–ethanol it was dried under vacuum at 100° for 12 hr.

Solvents used were purified as previously described.[1] 1,2-Dimethoxyethane was refluxed with sodium, then refluxed and distilled from lithium aluminum hydride, and finally passed through a column of acid-washed alumina. Acetonitrile (anhydrous), from Eastman Organic Chemicals, was twice refluxed and distilled from phosphorus pentoxide. Acetonitrile treated this way still contains sufficient ammonia ($ca.$ 10^{-6} M)[33] to be responsible for the decomposition of TBF observed in this solvent. Further distillation from a small quantity of sulfuric acid gave acetonitrile, b.p. 81.8° at 755 mm., which gave no decomposition of TBF up to about 1.5 hr. at 50°. In kinetic runs the concentration of catalyst was adjusted to cause completion of the runs within this time.

t-Butylperoxy Formate-d. t-Butylperoxy formate may be prepared by reaction of t-butyl hydroperoxide with acetic formic anhydride (from formic acid with ketene) or with formic acid directly.[34] The former method is prefered for small-scale economical use of formic-d acid.

Formic-d acid, 2.5 g., was cooled in an ice bath and a stream of ketene (prepared by pyrolysis of acetone and then passed through several traps cooled to $-25°$) was bubbled through until ($ca.$ 25 min.) infrared spectral analysis indicated, by loss of broad absorption of formic-d acid at 3000 cm.$^{-1}$, complete reaction. The acetic formic-d anhydride formed was cooled to 0°, 3.0 g. of t-butyl hydroperoxide added dropwise, and the mixture was allowed to stand at room temperature for 18 hr. Petroleum ether (b.p. 30–60°), 50 ml., was added and the solution was washed with 30 ml. of water in 5-ml. portions and then dried with magnesium sulfate. Evaporation and distillation gave 1.8 g. of t-butylperoxy formate-d, b.p. 43° at 22 mm., n^{25}D

1.3957 (lit. b.p. 41–42° at 22 mm., n^{25}D 1.3973 for normal TBF).[1] By infrared analysis this preparation was free from t-butyl hydroperoxide and t-butyl alcohol, the usual impurities in preparations of TBF. TBF-d possesses infrared absorption at 3000, 2200, 1735, 1693, 1460, 1390, 1370, 1250, 1190, 1110, 1025, 980, 860, 775, and 750 cm.$^{-1}$. TBF has a similar spectrum with all the above bands except those at 2200, 1735, 1693, and 980 cm.$^{-1}$, and has instead carbonyl absorption at 1760 cm.$^{-1}$ and absorption at 1070 and 850 cm.$^{-1}$. The bands at 1693 and 1735 cm.$^{-1}$ in TBF-d persist in dilute solution, as in kinetic runs in various solvents, and with roughly the same intensities.

Kinetic Procedure. Kinetic studies were carried out, as described earlier,[1] by measuring the loss of carbonyl absorption of TBF and TBF-d. Second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the concentration of base in the run. The concentration of peroxide in the runs varied from 0.02 to 0.04 M while the concentration of pyridine or triethylamine was less than 0.05 (except for runs in Table II). For weak bases higher concentrations were required, up to 0.6 M for o-nitroaniline. The runs for the kinetic isotope effects were usually carried out in pairs, one run for TBF, one for TBF-d, and with identical solutions of the base catalyst. This eliminated the effect on the k_H/k_D ratio of slight variation in base concentration possible in completely independent runs. However, the average deviations given in Table I are for independent runs with variation of the base concentration by two- to fourfold. Paired runs on TBF and TBF-d gave the ratios listed, but with less deviation than given in Table I.

Quinone (0.05 M) was added to 1,2-dimethoxyethane to inhibit induced free-radical decompositions. In runs with higher base concentration induced decomposition was sufficiently inhibited by the oxygen present in the sample tubes. TBF in 1,2-dimethoxyethane or acetonitrile containing only the perchlorate salts used in the salt effect studies was not decomposed over long periods of time. No direct reaction of these salts with TBF occurs.

(33) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3930 (1961).
(34) C. Rüchardt and R. Hecht, in press. Private communication from C. Rüchardt.