

greater than 99% by v.p.c. analysis). Nortricyclanone was prepared by the procedure of Meinwald.<sup>22</sup>

**Mass Spectra.** All spectra were taken on a Hitachi Model RMU-6D spectrometer with source temperature of 250° and inlet system at 150°. Variation of the

(22) J. Meinwald, J. Crandall, and H. E. Hymans, *Org. Syn.*, submitted. We wish to thank Professor Meinwald for a preprint of this procedure.

inlet temperature between 50 and 250° did not cause the spectra to change significantly.

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## Reactions in Frozen Solutions. II. Base-Catalyzed Decomposition of *t*-Butylperoxy Formate in Frozen *p*-Xylene

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The 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate (TBF) to yield carbon dioxide and *t*-butyl alcohol in *p*-xylene is accelerated at 0° by factors of 30 to 400 (depending on initial concentrations) when the solution is frozen. The reaction rate does not depend on the manner in which solutions are frozen. The frozen solution reaction, which is first order in TBF, is first order in base catalyst at low base concentration but becomes zero order in base at high base concentration. The reaction has a maximum rate at ca. 2° and occurs to as low a temperature as -30°. The presence of any soluble compound such as benzene, *o*-xylene, *m*-xylene, carbon tetrachloride, or heptane results in the same decrease per mole in observed rate constant. The results indicate that the reaction occurs in liquid regions, present in the frozen solutions, which contain a constant total concentration of solutes. Assuming ideal solutions, the dependency of the observed, first-order rate constants on the concentration of reactants, on temperature, and on the presence of impurities is given by the relationship  $k_{obsd} = k_2 C_h (B_0 / (B_0 + P_0 + I_0))$  where  $k_2$  is the normal, second-order rate constant for reaction in solution,  $C_h$  is the total solute concentration of liquid regions in the frozen solution, and  $B_0$ ,  $P_0$ , and  $I_0$  are the initial solution concentrations of base, peroxide, and impurities. Several general aspects of reactions in frozen solutions are discussed.

A bimolecular reaction which occurs in solution at low reactant concentrations would not generally be expected to proceed when the solution is frozen.<sup>1</sup> The greatly decreased mobility of the solid state should prevent the necessary mutual approach of the reaction components. Recent reports,<sup>2-4</sup> however, have in-

(1) For reviews and discussions of reactions in organic solids see, e.g., H. Morawetz, "Physics and Chemistry of the Organic Solid State," Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 287; Vol. 2, 1965, p. 853; J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 403; C. E. H. Bawn, "Chemistry of the Solid State," W. E. Garner, Ed., Butterworth and Co. (Publishers) Ltd., London, 1955, p. 254.

(2) (a) T. C. Bruice and A. R. Butler, *J. Am. Chem. Soc.*, **86**, 313 (1964); (b) *ibid.*, **86**, 4104 (1964).

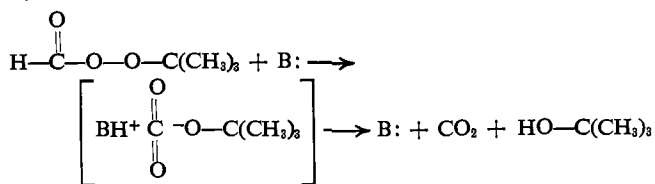
(3) N. H. Grant, D. E. Clark, and H. E. Alburn, *ibid.*, **83**, 4476 (1961).

dicated that some bimolecular reactions in dilute aqueous solutions may occur, and are even accelerated, when the solution is frozen. Bruice and Butler<sup>2</sup> in a study of the acid- and base-catalyzed hydrolysis of acetic anhydride in water and in ice have presented evidence that in frozen solutions the reaction components are gathered together in regions which remain liquid. The greater concentrations of reactants in these pockets of liquid result in an acceleration of the reaction. Other striking effects were also observed,<sup>2b</sup> as in the reaction of some thiolactones with morpholine where freezing of aqueous solutions causes a change in kinetic order as well as an acceleration of the reaction.

As has been pointed out,<sup>2-4</sup> rather special effects might appear with reactions in ice, but accelerated reactions have also been observed when dilute organic solutions are frozen.<sup>5</sup> In inert organic solvents, which are not involved in the stoichiometry of the reaction, the results are so far adequately explained by the concentration effect. The reactions are not actually solid-state reactions but involve highly concentrated solutes present in liquid regions among the crystalline solid. In this paper, the details of the pyridine- and 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate in frozen *p*-xylene solutions are presented and the general features of such "frozen state" reactions are discussed.

### Results

In organic solutions the base-catalyzed decomposition of *t*-butylperoxy formate (TBF) is a simple bimolecular reaction involving attack by base on the formate hydrogen.<sup>6</sup> A dipolar transition state is formed and



(4) W. H. Prusoff, *Biochim. Biophys. Acta*, **68**, 302 (1963).

(5) R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **87**, 2072 (1965).

(6) (a) R. E. Pincock, *ibid.*, **86**, 1820 (1964); (b) *ibid.*, **87**, 1274 (1965).

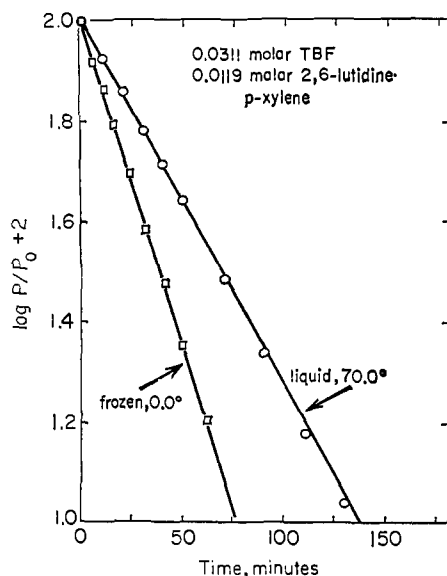


Figure 1. First-order plots for 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate in *p*-xylene at 0° (frozen) and at 70° (not frozen) using identical samples.

the final products are carbon dioxide and *t*-butyl alcohol.

The same products are formed by reaction in frozen solutions. A solution of 0.347 *M* TBF and 0.0758 *M* pyridine in *p*-xylene, frozen in liquid nitrogen and held at 0° for 24 hr., resulted in 92% carbon dioxide and 96% *t*-butyl alcohol, while 4% of the TBF was undecomposed. The same solution held unfrozen at *ca.* 15° (the melting point of pure *p*-xylene is 13.26°) for 24 hr. was 50% decomposed, close to the expected value as extrapolated from rates in solution at higher temperatures. At lower concentrations of reactants, formation of *t*-butyl alcohol and carbon dioxide in frozen solutions was also indicated by infrared analysis of kinetic-run samples.

For kinetic studies the reaction in dilute, frozen solutions was sufficiently accelerated in the frozen state to allow quenching simply by defrosting the samples of a run. Measurement of peroxide concentration was then carried out at room temperature.<sup>6a</sup> Figure 1 shows first-order plots for 2,6-lutidine-catalyzed TBF decomposition in liquid *p*-xylene at 70° and in frozen *p*-xylene at 0° using identical samples. The frozen state kinetic runs were always, as with liquid solutions studied earlier,<sup>6</sup> first order in peroxide at all concentrations of base or TBF. Runs were followed for 2–4 half-lives with no deviation of the plots from the log (relative peroxide concentration) vs. time relationship.

The reaction in individual samples of a run and the observed rate constants were not affected by the volume of sample, by surface or volume of added insoluble material, or, surprisingly, by the manner in which the samples were frozen. Figure 2 shows the results for two widely different freezing methods, relatively large samples frozen slowly over several minutes by seeding at 8° and small samples frozen immediately by immersion in liquid nitrogen. Different macroscopic distributions of the crystalline samples were readily apparent from the different relative transparency of the solid *p*-xylene as frozen these two ways, but the ob-

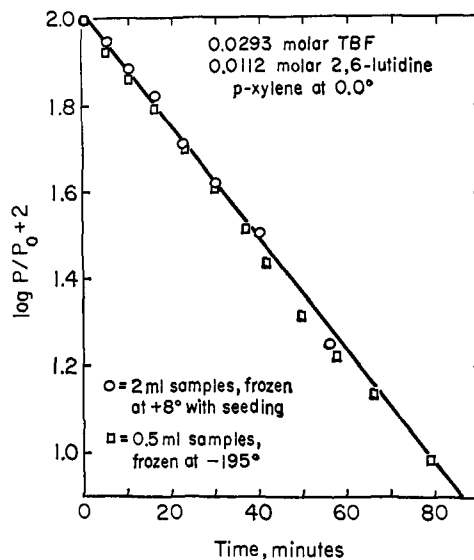


Figure 2. First-order plot for 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate in frozen *p*-xylene at 0° in samples initially frozen at –195 and 8°.

served rates were the same when the samples were brought to 0° for the kinetic run. This insensitivity to many variables in preparation of frozen samples is distinctly contrary to results for true solid state reactions.<sup>1</sup> For this frozen state reaction, as in ordinary solution kinetics, the relevant variables are the concentrations of reactants, the temperature of the run, and the purity of the solvent. These were considered in turn as follows.

**Effect of Concentration.** The results of variations in the initial concentration of base and of TBF for kinetic runs in frozen *p*-xylene solutions at 0° are given in Table I. The peroxide concentration of the solutions was usually from 0.025 to 0.03 *M*, while the base concentration was varied from  $3.8 \times 10^{-4}$  to 0.3 *M*.

It is especially remarkable that with a low concentration of 2,6-lutidine ( $3.8 \times 10^{-4}$  *M*) the base is not “lost” when the solution is frozen, but retains its catalytic efficiency to completely decompose the TBF at some 60-fold greater solution concentration. Comparisons of rates in unfrozen solutions at the lowest concentration of base catalyst to rates when the solution is frozen shows that the base is relatively most efficient at low concentrations. Thus the  $k_{\text{obsd}}$  for  $3.8 \times 10^{-4}$  *M* lutidine is 400 times greater than the calculated rate constant for reaction at 0° in a solution of this concentration; at 0.14 *M* lutidine the observed rate constant in frozen samples is only 30 times greater than the rate constant for reaction in solution.

The kinetic data of Table I may be summarized by stating that at constant peroxide concentration and at low lutidine concentrations the observed rate constants are nearly proportional to the lutidine concentration; at high lutidine concentrations the observed rate constants become independent of lutidine concentration (see Figure 4). That is, the observed kinetic order changes from first order to zero order in lutidine as the lutidine concentration is increased. A similar result is found with pyridine as catalyst.

When the lutidine concentration is held constant, and the peroxide concentration is increased, the ob-

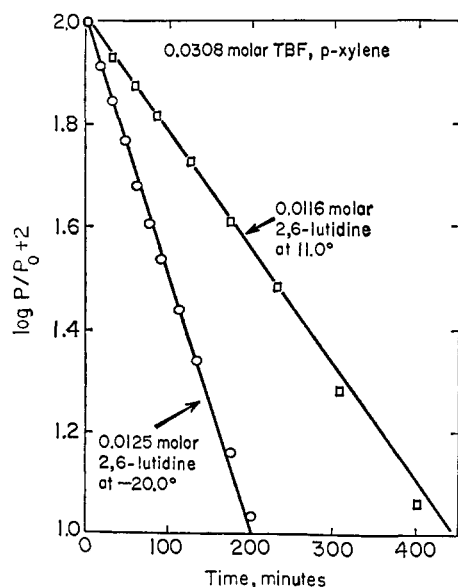


Figure 3. First-order plots for 2,6-lutidine-catalyzed decomposition of *t*-butylperoxy formate in frozen *p*-xylene at 11 and  $-20^{\circ}$ .

served rate constants decrease. This occurs even though the individual runs were always first order in TBF throughout several half-lives. These odd kinetic effects are discussed below.

**Effect of Temperature.** The rate of reaction of 2,6-lutidine with TBF in frozen *p*-xylene shows an amazing

Table I. Observed Rate Constants for Base-Catalyzed Decomposition of TBF in Frozen *p*-Xylene at  $0^{\circ}$

Concn. of TBF, $M \times 10^2$	Concn. of base, $M \times 10^2$	$k_{\text{obsd}} \times 10^6$ , $\text{sec.}^{-1}$
2,6-Lutidine Catalyzed		
2.57	0.0386	2.69
2.88	0.0773	4.82
2.95	0.154	9.09 <sup>a</sup>
2.95	0.154	9.39 <sup>b</sup>
2.85	0.249	14.6
2.84	0.535	26.9
3.12	0.869	39.6
2.82	1.13	44.4
2.93	1.12	46.2 <sup>b</sup>
2.93	1.12	50.2 <sup>a</sup>
2.93	1.63	60.8
3.05	2.06	62.4
2.84	2.58	74.6
2.93	3.52	79.7
3.05	4.98	77.0
2.82	7.50	85.7
3.03	14.1	74.6
27.4	0.579	3.61
29.2	1.49	9.09
Pyridine Catalyzed		
2.97	0.314	2.31
2.75	1.04	7.36
2.95	2.08	11.0
3.26	3.13	13.6
2.62	4.62	18.4
2.62	8.46	19.9
2.83	15.2	21.4
2.92	15.0	19.3
2.82	20.8	19.9
3.14	26.4	21.8
2.82	31.3	19.9
28.5	14.2	6.56

<sup>a</sup> Samples of run frozen at  $-195^{\circ}$  <sup>b</sup> Frozen at  $8^{\circ}$ .

Table II. Observed Rate Constants for 2,6-Lutidine-Catalyzed Decomposition of TBF at Various Temperatures in Frozen *p*-Xylene

Concn. of TBF, $M \times 10^2$	Concn. of 2,6-lutidine, $M \times 10^2$	Temp., $^{\circ}\text{C.}$	$k_{\text{obsd}} \times 10^5$ , $\text{sec.}^{-1}$
3.11	1.19	12.0	2.9 <sup>a</sup>
3.08	1.16	11.0	8.56
3.08	1.19	10.0	13.8
3.09	1.25	8.0	23.1 <sup>b</sup>
3.08	1.19	6.0	33.5
3.08	1.19	4.0	39.2
3.08	1.19	2.0	52.4
3.08	1.19	0.0	47.6
3.11	1.19	0.0	50.2 <sup>c</sup>
3.12	0.87	0.0	39.6 <sup>d</sup>
3.05	1.16	$-10.0$	36.1 <sup>e</sup>
3.09	1.25	$-20.0$	19.3 <sup>b</sup>
3.05	1.16	$-30.0$	7.61 <sup>e</sup>
3.12	0.87	$-10.0$	29.6 <sup>d</sup>
3.14	1.74	$-10.0$	47.2
3.14	3.37	$-10.0$	66.0
Unfrozen Solutions			
3.08	1.16	50.0	8.76
3.11	1.19	70.0	28.2 <sup>c</sup>
3.10	1.04	90.0	74.5
2.72	0.21	90.0	14.6
3.09	2.08	90.0	137

<sup>a</sup> Reaction not followed to completion, initial rate constant. <sup>b-c</sup> Denote paired runs using same solutions at different temperatures.

temperature dependence. Table II presents the data for runs in the frozen state from 12 to  $-30^{\circ}$  at constant initial concentrations, as well as runs at 50, 70, and  $90^{\circ}$  in liquid *p*-xylene.

The observed rate constant in frozen solutions increases by a factor of 18 on decreasing the temperature from 12 to  $2^{\circ}$ . However, at *ca.*  $2^{\circ}$  a further decrease in temperature begins to lower the rate. At  $-30^{\circ}$  the reaction still occurs at an easily measurable rate, but at  $-70^{\circ}$  no loss of peroxide occurs over long periods. Figure 3 shows that the runs remain first order in TBF and also illustrates that the reaction is faster at  $-20^{\circ}$  than at  $11^{\circ}$ . From runs in liquid at 50, 70, and  $90^{\circ}$  the activation parameters for the second-order reaction of TBF with 2,6-lutidine are  $\Delta H^*$  12.3 kcal. and  $\Delta S^*$   $-30.5$  e.u.

**Effects of Impurities.** The kinetic results of addition of various compounds to the thrice-recrystallized *p*-xylene used as solvent are given in Table III. The rate is depressed by such neutral compounds as benzene, *o*-xylene, *m*-xylene, heptane, and carbon tetrachloride. At low concentrations of peroxide and of lutidine, the rate is extremely sensitive to the presence of these impurities. At the concentration of reactants given in Table III,  $1.5 \times 10^{-2}$  *M* benzene (one molecule per 500 of solvent) decreases the rate by one-half. A dampening of this effect is shown in that  $5.7 \times 10^{-2}$  *M* benzene is required to bring about another decrease by one-half. It is significant that, with the exceptions of *t*-butyl alcohol and anthracene, all the compounds tested were nearly equally effective in depressing the rate. Anthracene had no effect on the rate, and *t*-butyl alcohol at relatively high concentrations caused a small decrease in  $k_{\text{obsd}}$ . The observed kinetic effects of these compounds constituted a test which showed that the reaction in the frozen TBF-lutidine-*p*-xylene

**Table III.** Observed Rate Constants at 0° for 2,6-Lutidine-Catalyzed Decomposition of TBF<sup>a</sup> in Frozen *p*-Xylene Containing Added Compounds

Substance	Concn., $M \times 10^2$	$k_{\text{obsd}}$ $\times 10^6$ , sec. <sup>-1</sup>
None	...	48.1 <sup>b</sup>
Benzene	0.898	32.5
Benzene	1.49	24.1
Benzene	2.84	17.8
Benzene	5.71	10.3
<i>o</i> -Xylene	1.16	28.9
<i>m</i> -Xylene	1.19	28.9
Anthracene	1.51	48.7
2,6-Di- <i>t</i> -butyl- <i>p</i> - cresol	1.99	17.0
<i>t</i> -Butyl alcohol	3.32	33.2
Heptane	3.68	10.2
Carbon tetrachloride	4.31	11.5 <sup>b</sup>
Carbon tetrachloride	4.73	11.1 <sup>b</sup>
None	...	46.3 <sup>b</sup>

<sup>a</sup> Concentration of TBF 0.030 *M*, of 2,6-lutidine 0.012 *M*.

<sup>b</sup> Different batches of solvent.

system does proceed in unfrozen regions of high reactant concentration.

### Discussion

As outlined in the introduction, a general explanation for the observed reactions in frozen solutions involves the existence of liquid regions, scattered throughout the pure crystalline solvent, containing high concentrations of reactants. Any reaction higher than first order, whose components are soluble in the liquid solvent and insoluble in the crystalline solvent below the temperature of freezing, should experience an acceleration when the system is frozen. Basic to any treatment of such reactions is the requirement that the liquid "holes" in a frozen solution must all contain the same constant total concentration of solutes. Although the average volume of the holes might reasonably be expected to depend on the method of freezing, with a greater number of smaller holes formed on fast freezing, a constant solute concentration is required in the unfrozen regions by the phase equilibrium between solution and pure solid.

This requirement of constant total concentration in the liquid regions introduces an interesting variable to the kinetic treatment of frozen state reactions. While kinetics in dilute solutions ordinarily involve changes in moles at constant volume per unit of time, a frozen solution reaction may involve changes in moles and in reaction volume per unit of time. At constant temperature, the total volume of liquid regions is set by the total number of moles which must be accommodated. As the total moles increase or decrease the walls of the regions melt or freeze to readjust to the required constant concentration of solutes. The total reaction volume will then be different for separate frozen kinetic runs at different initial solution concentrations. Even during a single run the total reaction volume may change if the number of moles of products is different than the number of moles of reactants, or if the products are insoluble.<sup>7</sup> Such changes in volume make reactions in frozen solutions

(7) This assumes that phase equilibrium is rapidly attained throughout the course of a reaction.

more analogous to gas phase reactions at constant pressure than to solution reactions at constant volume.

The qualitative aspects of rates of reactions in frozen solutions may be visualized, as applied below for the TBF-base reaction in frozen *p*-xylene, in terms of two factors: variable volumes of liquid regions containing constant total concentration and different relative reactant concentrations in these regions. Experimentally obtained rates, however, are measured in terms of moles/liter of solution (*i.e.*, the concentration is measured after defrosting) and not in terms of the volume or the concentration of the liquid regions in frozen solutions. The observed rate constants may be related to the known solution concentrations as follows<sup>8</sup>: rate in liquid regions =  $k_2 P_h B_h$ ; rate in solution (after defrosting) =  $dP_s/dt = -k_2 P_h B_h \cdot V_h/V_s$ . Assuming that all the solutes are present in the liquid regions of a frozen solution, then  $P_h V_h = P_s V_s$ ;  $B_h V_h = B_0 V_s$ ;  $C_h V_h = (P_s + B_0 + I_0 + [\text{prod}]_s) V_s$ .

In terms of the amount reacted, if the equivalent of 1 mole of product is derived from 1 mole of peroxide (see discussion below) then  $P_s = (P_0 - x)$  and  $x = [\text{prod}]_s$ . Substitution and integration gives  $\ln(P_0 - x)/P_0 = -[k_2 C_h B_0/(B_0 + P_0 + I_0)]t$ .

The observed rate constant in terms of initial solution concentrations is then eq. 1.

$$k_{\text{obsd}} = k_2 C_h \frac{B_0}{B_0 + P_0 + I_0} \quad (1)$$

In the decomposition of TBF in frozen *p*-xylene, changes in reaction conditions by variation of base, peroxide or "impurity" concentrations, or by variation in temperature, all result in changes in the observed rate constants according to eq. 1.

**Concentration of Reactants.** Figure 4 shows the observed pseudo-first-order rate constants at 0° for 2,6-lutidine- and pyridine-catalyzed decomposition of TBF (at near constant TBF concentration) as a function of base concentration.<sup>9</sup> The relationship predicted from eq. 1 (in the form  $k_{\text{obsd}} = k_{\text{obsd}}(\text{high base}) B_0/(B_0 + P_0)$ ) is given by the curved lines. The change in observed kinetic order from first order in base at low base concentrations to zero order in base at high base concentrations arises from the changing ratio of base to total solute concentration. At low base concentrations the liquid regions in which the frozen solution reaction proceeds are filled predominately with TBF, and an increase in base concentration does not appreciably increase the reaction volume. However, as the absolute concentration of base in the liquid regions is increased, the rate of the reaction is also proportionately increased and the reaction appears to be first order in base as well as in TBF.

On the other hand, at high base concentrations where the liquid regions are filled predominantly with the base, a further increase in base concentration of the

(8) The notation used is as follows:  $P_h, B_h, P_s, B_s$  are concentrations of the peroxide and of base in liquid regions of frozen solutions and in defrosted solutions, respectively;  $V_h$  and  $V_s$  are total volumes of the regions and of defrosted solutions;  $P_0, B_0$ , and  $I_0$  are initial solution concentrations of peroxide, base, and any soluble impurity, respectively;  $C_h$  is the total constant concentration of solutes in the liquid regions;  $[\text{prod}]_s$  is the solution concentration of soluble products of the reaction; and  $k_2$  is the normal, second-order rate constant for bimolecular reaction in solution.

(9) The greater catalytic effect of lutidine is expected from its greater basicity. See ref. 6b.

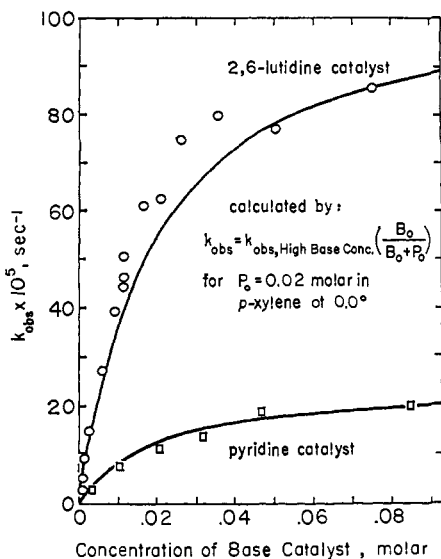


Figure 4. Relation of observed first-order rate constants to the base concentration for 2,6-lutidine- and pyridine-catalyzed decomposition of *t*-butylperoxy formate in frozen *p*-xylene at 0°. The values of  $k_{\text{obsd}}$  (high base concentration) used to calculate the curves were  $120 \times 10^{-5} \text{ sec}^{-1}$  for 2,6-lutidine and  $24.7 \times 10^{-5} \text{ sec}^{-1}$  for pyridine as catalyst.

initial solutions serves only to enlarge the reaction volumes in the frozen solutions. The base concentration in the reaction regions remains constant, the first-order rate constant remains the same, and the reaction appears to be zero order in base concentration.

If runs at constant base concentration but different peroxide concentrations are compared the rate constants observed (see Table I) decrease with increasing peroxide concentration. The presence of greater peroxide concentration in an unfrozen solution results in a greater volume of liquid regions in a frozen solution. This larger volume dilutes the available base down to a lower concentration and the observed rate constant is correspondingly decreased.

**Temperature Dependence.** The striking temperature dependence of this frozen solution reaction at constant initial reactant concentrations results from a competition between two factors. The second-order rate constant for bimolecular reaction in solution decreases with a decrease in temperature ( $\Delta H^* = 12.3 \text{ kcal.}$  and  $\Delta S^* = -30.5 \text{ e.u.}$ ), but the concentrations of the liquid regions in frozen solutions increase with a decrease in temperature. As a consequence the rate shows a maximum at several degrees below the freezing point of the solution. Figure 5 is a plot of  $\log k_{\text{obsd}}$  against  $1/T$  for reaction in liquid and in frozen solutions at constant initial concentrations. The curved line is calculated from the relationship  $k_{\text{obsd}} = k_2 C_h$ , where  $k_2$  is obtained by extrapolation of the rates observed in liquid solutions at 90, 70, and 50° and  $C_h$  is obtained from measurements of the concentration of 2,6-lutidine required to prevent freezing of *p*-xylene at various temperatures<sup>10</sup> (i.e., from the phase equilibria of the *p*-xylene-2,6-lutidine system, see Figure 7).<sup>11</sup> From the correspondence of the

(10) The concentrations of the liquid regions at different temperatures in frozen solutions, and some volume changes, may be roughly measured by n.m.r. spectroscopy (see Experimental) as well as from freezing point-composition measurements.

(11) In the absence of the experimentally determined total concen-

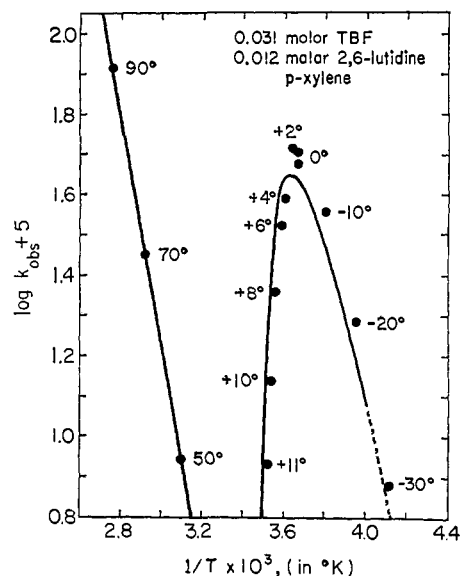


Figure 5. Temperature dependence of observed rate constants for constant *t*-butylperoxy formate and 2,6-lutidine concentrations (curved line is calculated from  $k_{\text{obsd}} = k_2 C_h$ ).

observed rate constants with the theoretical curve shown in Figure 5 it is apparent that the form of the observed temperature dependence is well reproduced by the relationship  $k_{\text{obsd}} = k_2 C_h$ . The magnitude of the calculated, first-order rate constants are not, however, given directly by this relationship but should be modified by the ratio of base concentration to total solute concentration (see eq. 1). When this is done the calculated rate constants are less by a factor of about 5 than the experimental rate constants. This discrepancy may be due to a change in relative reactant concentrations in the liquid regions from that expected from relative concentrations in unfrozen solutions or it may be caused by an increase in rate due to a solvent effect.<sup>12</sup> Since the reaction regions contain high concentrations of TBF and 2,6-lutidine, the  $k_2$  as measured in dilute solutions and extrapolated from higher temperatures cannot be strictly applicable.

**Effect of Impurities.** Figure 6 presents the effects of addition of various compounds to frozen kinetic runs at constant initial TBF and base concentrations. For soluble compounds a decrease in rate is expected as the reaction volumes increase to incorporate the otherwise inert compound.<sup>13</sup> For ideal solutions, the observed decrease in rate should depend only on the concentration and not on the structure of the added compound. This ideal behavior of *o*-xylene, *m*-xylene, benzene, and carbon tetrachloride as solutes in *p*-xylene was shown separately by freezing point-composition measurements down to  $-5^\circ$  (see Figure 7). All of these compounds are equally able to depress the

tration, the temperature dependence may be calculated from the activation parameters for liquid phase reaction together with the concentration obtained according to ideal solution behavior from the molar heat of fusion and the freezing point of pure solvent.

(12) Since both TBF and 2,6-lutidine are more polar than *p*-xylene, an increase in reaction rate at high solute concentration (analogous to the increase observed<sup>6b</sup> for high pyridine concentrations in heptane as solvent) might be expected.

(13) A saturated solution of anthracene in *p*-xylene does not have a freezing point less than  $13^\circ$ . No anthracene can be dissolved in liquid *p*-xylene at  $0^\circ$  and no effect on the rate of TBF reaction in frozen *p*-xylene is expected nor observed.

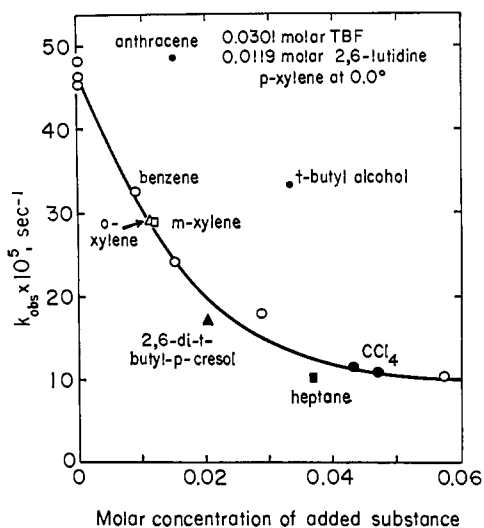


Figure 6. Changes in observed rate constant, at constant *t*-butylperoxy formate and 2,6-lutidine concentrations, caused by addition of various compounds.

freezing point of *p*-xylene. The rate depression given by these compounds is somewhat greater than predicted from the relation  $k_{\text{obsd}} = k_{\text{obsd}(\text{no impurity})} \cdot (B_0 + P_0)/(B_0 + P_0 + I_0)$  derived from eq. 1. This might be due to relatively lower concentrations of base or peroxide in the liquid regions than expected from initial solution concentrations. The impurity would then be at relatively higher concentration and the  $k_{\text{obsd}}$  further decreased.

*t*-Butyl alcohol is much less capable of depressing the rate of reaction of TBF with 2,6-lutidine in frozen *p*-xylene or of depressing the freezing point of *p*-xylene than are the compounds mentioned above (see Figures 6 and 7). These observations are related, of course, and consistent with the expected self-association of *t*-butyl alcohol by hydrogen bonding. This factor fortunately makes the TBF–base reaction simpler than might be expected. The stoichiometric production of 2 moles of products (carbon dioxide and *t*-butyl alcohol) from 1 mole of TBF should result in an enlargement of the reaction volume during a kinetic run. However, carbon dioxide is not highly soluble in *p*-xylene at low temperatures<sup>14</sup> and *t*-butyl alcohol is associated. The assumption that 1 mole of soluble products forms from 1 mole of TBF is required in order to obtain eq. 1.<sup>16</sup> This approximation seems reasonable, and is consistent with the observation of straight, first-order kinetic plots.

The form of the rate depression caused by various amounts of impurities at constant reactant concentrations as illustrated in Figure 6 is consistent with eq. 1. Another way of illustrating the effect of impurities is shown in Figure 8 where rates in pure and in impure solvents are compared over a range of base concentrations. As is predicted by the relationship  $k_{\text{obsd}}$

(14) For comparison, the solubility of carbon dioxide at 1 atm. in toluene at 0° is *ca.* 0.14 *M*.<sup>16</sup> This is considerably less than the 2.35 *M* concentration of solutes in the reaction regions at 0° (see Figure 7).

(15) D. L. Williams, U. S. Atomic Energy Commission, L.A.-1484, 1952; see *Chem. Abstr.*, 47, 12008 (1953).

(16) This is equivalent to the assumption that the total reaction volume during a run remains constant. In the reaction of triethylamine with methyl iodide in frozen benzene solutions, the reaction volume decreases during a run as the insoluble product is formed: T. E. Kiovsky, unpublished observations.

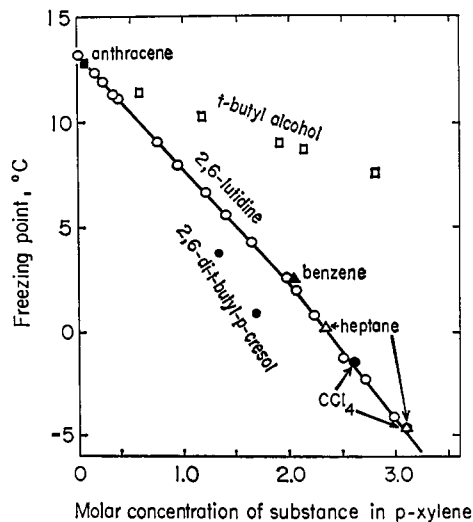


Figure 7. Relation of freezing point of *p*-xylene solutions to the concentration of various solutes.

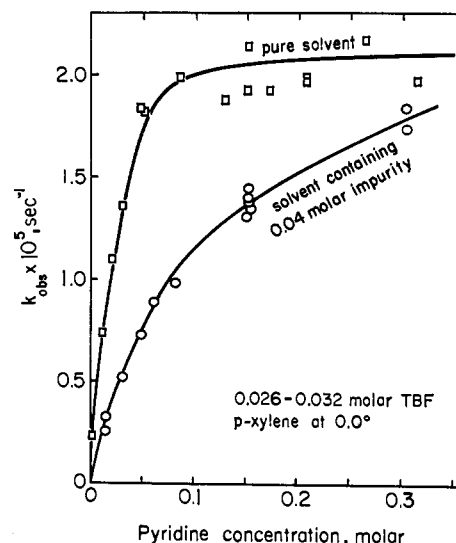


Figure 8. Effect of impurities (*ca.* 0.04 *M*) on the observed rate constant for reaction of *t*-butylperoxy formate with pyridine in frozen *p*-xylene at various concentrations of pyridine.

$= k_{\text{obsd}(\text{no impurity})} (B_0 + P_0)/(B_0 + P_0 + I_0)$  the effect of impurities is greatest at low reactant concentrations. At high reactant concentrations the rate in impure solvent is the same as in pure solvent.

**Summary.** The kinetic features of reactions in frozen systems,<sup>2-5</sup> as illustrated here for the TBF–base reaction in *p*-xylene, include variation in kinetic order at different initial solution concentrations, great sensitivity to impurities, and insensitivity to the method of freezing. If a bimolecular reaction has a low activation energy the decrease in temperature necessary to freeze the solution is easily compensated for by the increase in concentration. For reactions of soluble compounds there is then considerable kinetic acceleration at an optimum temperature below the freezing point of the solution.

The presence of liquid regions in apparently completely frozen samples of a solution and the possible occurrence of some reactions in these regions at temperatures far below the freezing point of the solution

should often be considered. At least for simple systems, like the reaction studied here, treatment of frozen state reactions in terms of ideal solutions leads to kinetic equations which fit the observed results.

### Experimental

**Materials.** 2,6-Lutidine (Eastman Organic Chemicals practical grade) was refluxed with methyl *p*-toluenesulfonate, then distilled and redistilled from barium oxide. The sample used had f.p.  $-6.5^\circ$  (lit. f.p.  $-6.9$ ,<sup>17</sup>  $-6.07$ ,<sup>18</sup>  $-5.9$ ).<sup>19</sup> Reagent grade pyridine was refluxed with barium oxide and distilled.

*p*-Xylene (m.p.  $12-13^\circ$ , Eastman Organic Chemicals) was purified by slow crystallization of about one-half of the total volume of liquid. After decanting the liquid, the solid was melted and the crystallization procedure was repeated three times. This *p*-xylene was then refluxed with sodium and distilled. *p*-Xylene was analyzed by vapor phase chromatography on a 10% Bentone 34-10% diisodecyl phthalate on 60-80 Chromosorb W column at  $88^\circ$ . In several purified batches no impurities were detected (e.g., *o*-xylene was less than 0.1 mole %). A good measure of purity is the freezing point range. The thrice-recrystallized *p*-xylene froze to over 90% with a  $0.2^\circ$  range. The maximum total impurity is then less than 0.1 mole %.<sup>20</sup> The rate of the TBF-2,6-lutidine reaction was the same with different batches of *p*-xylene which had been recrystallized various times. Eastman reagent grade *p*-xylene used directly gave rates ca. 30% lower than purified solvent; other commercial reagent grade *p*-xylene showed higher impurity concentrations by v.p.c. or freezing point analysis, and gave still lower rates in frozen kinetic runs.

*t*-Butylperoxy formate was prepared as previously described,<sup>6</sup> and stored in polyethylene bottles at ca.  $0^\circ$  to avoid the slow decomposition caused by glass. The melting point of TBF is less than  $-70^\circ$ ; the purest samples when frozen in liquid nitrogen remelted when brought to  $-70^\circ$ .

**Kinetic Studies.** Solutions were usually made up by adding a known freshly prepared solution of 2,6-lutidine (or pyridine) in *p*-xylene to a weighed quantity of TBF and then diluting to 25 ml. with *p*-xylene. The solution was divided in volumes of 1-2 ml. into about ten to fifteen glass ampoules. The ampoules were sealed under air at atmospheric pressure and frozen, usually by dumping them into a Dry Ice-acetone mixture. Two or three unfrozen samples were retained for controls as described below. No special techniques for sample preparation were necessary. There was no difference in rate of TBF decomposition in frozen samples which differed in any of the following ways: presence of insoluble materials; different volumes of solution; degassed or not degassed; and samples frozen by placement in baths at 8 or  $0^\circ$  (with seeding), at  $-70^\circ$ , or at  $-195^\circ$ .

The frozen samples were placed in a constant temperature bath and, after allowing a few minutes for

temperature equilibration, the "zero time" sample was withdrawn. This was quickly defrosted, usually by shaking under tap water at room temperature. Other samples were collected similarly at various times and all were stored at room temperature until analysis as described below. In runs at high base concentrations the decomposition at room temperature was sufficiently fast to require either immediate analysis when each sample was defrosted or storage at ca.  $-70^\circ$  until collection was complete and the analysis of all the samples could be carried out over a few minutes. In every run separate samples were stored frozen at  $-70^\circ$  (or  $-195^\circ$ ), unfrozen at room temperature, and, if possible, at the temperature of the run. The *p*-xylene solutions could be often retained as supercooled liquid samples at  $0^\circ$  for longer times than required for the run and the analysis. These samples were analyzed after the analysis of kinetic run samples was completed and, except as noted above at the highest base concentrations, were less decomposed than the "zero time" sample of the run.

The defrosted samples were analyzed by measurement of the infrared carbonyl absorption of TBF as described earlier.<sup>6a</sup> In every case plots of  $\log P/P_0$  vs. time followed usually to 80-90% decomposition were straight. Since infinity samples taken after 8-10 half-lives for various runs showed no absorption for TBF, the infinite time optical density for runs in which it was not measured was assumed to be zero. Observed, first-order rate constants for completely independent runs at similar concentrations sometimes varied by 10%, but there was no scatter of points in each individual run.

**Frozen Samples.** Frozen samples at the low solute concentrations used in these kinetic studies showed no visually apparent liquid phase. Nuclear magnetic resonance signals for 1 *M* TBF in *p*-xylene at 7.8 (solvent methyl groups) and  $\tau$  8.9 (TBF methyl groups) (ratio of areas 4.5 to 1.0) disappeared when the solution was frozen, but when the signal amplitude was increased by ca. 60 times, two broad peaks were apparent from ca.  $\tau$  7 to 10. If the sample was frozen quickly, the peaks were each nicely symmetrical and at  $0^\circ$  showed areas of 1.6 to 1.0 (i.e., 29.4 mole % TBF). The mole per cent obtained from freezing point measurements is 30 mole % TBF (2.35 *M*, see Figure 7). On decreasing the temperature to  $-5^\circ$ ,  $-10^\circ$ ,  $-15^\circ$ , and  $-30^\circ$  the *p*-xylene peak decreased while the area of the TBF peak remained constant. At  $-50^\circ$  the *p*-xylene had essentially disappeared relative to the TBF signal, which now was also of decreased intensity. These observations are taken as evidence of the presence of a liquid phase containing relatively greater concentrations of TBF as the temperature decreases. The broad character of the signals from frozen samples is due to different fields present at various positions of liquid phase in the frozen sample. Fast freezing produces a more homogenous distribution of liquid regions (symmetric n.m.r. peaks) than in samples frozen slowly (each n.m.r. peak was unsymmetrical).

Experiments concerning the distribution of solutes in frozen solutions were also carried out. As expected, TBF was more concentrated in the liquid portion of a partly frozen *p*-xylene solution. The incorporation

(17) J. A. Cathcart and D. D. Reynolds, *J. Am. Chem. Soc.*, **73**, 3504 (1951).

(18) H. C. Brown, S. Johnson, and H. Podall, *ibid.*, **76**, 5556 (1954).

(19) E. A. Coulson and J. I. Jones, *J. Soc. Chem. Ind. Japan*, **65**, 169 (1946).

(20) A. Weissberger and E. Proskauer, "Organic Solvents," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 37,76.

of TBF in the frozen portion of a two-phase system was less in the initial stages of freezing and less when the freezing was carried out slowly. It is unlikely that crystals of *p*-xylene directly incorporate any significant amount of TBF.

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## Relative Stability of Cyclic Olefins. I. Equilibrium Isomerization of Monocyclic Olefins Containing Four- to Six-Membered Rings<sup>1</sup>

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The equilibria of five groups of isomeric cyclomonoolefins having four-, five-, and six-membered rings and a one- or two-carbon side chain were measured at 25° over a sodium-alumina catalyst and at 250° over acidic alumina. Under these conditions the double bond migrates to all possible positions. Equilibrium constants, enthalpies, and free energies of isomerization were calculated. The equilibrium ratio methylenecycloalkane/1-methylcycloalkene has a minimum value for the five-membered ring compounds. The ethylenecycloalkane/1-ethylcycloalkene ratio at 25° is higher for the six- than for the five-membered ring series, but the relative order is reversed at 250°. The 1-alkylcycloalkenes are by far the most stable isomers in all series studied. Among the endocyclic isomers having a disubstituted double bond, the 3-alkyl isomer is more stable than the 4-alkyl isomer in the five-membered ring series, whereas the reverse is observed for the six-membered ring compounds. 3-Methylcyclobutene is very unstable with respect to the 1-alkylisomer ( $K^{25} \sim 8500$ ).

The variation with ring size of the stability of methylenecycloalkenes and 1-methylcycloalkenes has attracted considerable attention in recent years. In particular, the predictions of Brown and co-workers<sup>4</sup> as to the relative stability of *exo*- and 1-endocyclic olefins in the five- as compared with the six-membered ring series has led to some controversy. Turner and Garner<sup>5,6</sup> determined the heats of hydrogenation of pairs of such isomers having five- and six-membered rings and hence derived the enthalpies of isomerization. Subsequently,

(1) For preliminary communications see: (a) E. Gil-Av and J. Shabtai, *Chem. Ind. (London)*, 1630 (1959); (b) J. Herling and E. Gil-Av, *Bull. Res. Council Israel*, 10A, 78 (1961); (c) E. Gil-Av and J. Herling, *Tetrahedron Letters*, No. 1, 27 (1961); (d) J. Shabtai and E. Gil-Av, *ibid.*, No. 9, 467 (1964).

(2) On leave from the Weizmann Institute of Science, Rehovoth, Israel.

(3) To whom inquiries should be addressed.

(4) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, 76, 467 (1954).

(5) R. B. Turner and R. H. Garner, *ibid.*, 80, 1424 (1958), and references therein.

(6) R. B. Turner in "Theoretical Organic Chemistry," IUPAC Kekulé Symposium, Butterworth and Co. (Publishers) Ltd., London, 1959, p. 79.

accurate measurements of the equilibria at 25° under acid-catalyzed conditions were carried out by Cope and co-workers.<sup>7</sup>

As the latter authors used a relatively mild catalyst, *i.e.*, *p*-toluenesulfonic acid in acetic acid solution, migration of the double bond was observed between the *exo* and the 1-*endo* position only. In the present work, on the other hand, equilibration was carried out by employing as catalyst sodium on alumina<sup>8</sup> at room temperature and activated alumina at 250°. Under these conditions, migration of the double bond occurred to all available positions and a complete picture could thus be obtained of the relative stability of all olefinic isomers possible for a given ring size. Furthermore, measurements were extended to compounds having a four-membered ring, as well as to derivatives with a two-carbon side chain.

The cyclic olefins studied are listed in Tables I and II. The sodium-alumina catalyst did not cause any detectable side reactions at 25°, and carbon skeleton rearrangement did not exceed 1–5% on activated alumina at 250°. The data given in Tables I and II represent the average of a number of experiments, with approach to equilibrium being effected in most cases from different sides. Analysis of the equilibrated mixtures was carried out by gas-liquid chromatography (see Experimental).

The present results are in agreement with data of Cope and co-workers<sup>7</sup> as far as the equilibrium constants at 25° of the 1-*endo*-*exo* pairs of isomers in the five- and six-membered ring series are concerned. Further, the values of  $\Delta F^\circ$  calculated from the equilibrium constants are close to the corresponding  $\Delta H^\circ$  values determined by Turner and co-workers<sup>5,6</sup> from heats of hydrogenation. The significance of these findings has been amply discussed in the literature.<sup>4–7</sup>

Since the present data were obtained by equilibrium isomerization of the olefins in the form of pure liquids (or in a saturated hydrocarbon as solvent), it is evident that the possible association of the olefins with acetic

(7) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.*, 82, 1750 (1960).

(8) H. Pines and W. O. Haag, *J. Org. Chem.*, 23, 328 (1958); W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, 82, 387 (1960).