

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

## Effects of Nonpolar Solvents on an Ionic Reaction. The Ionic Decomposition of *tert*-Butylperoxy Formate

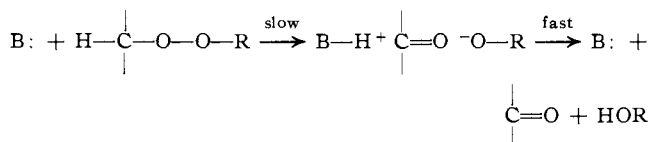
BY RICHARD E. PINCOCK

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*tert*-Butylperoxy formate undergoes relatively slow unimolecular thermal decomposition in chlorobenzene ( $\Delta H^\ddagger = 38$  kcal.,  $\Delta S^\ddagger = 15$  e.u.) and generates formyloxy and *tert*-butoxy radicals by simple breakage of the peroxide bond. In *n*-butyl ether a first-order induced decomposition occurs which involves attack by radicals on the peroxide oxygens. In the presence of pyridine a bimolecular ionic elimination reaction proceeds ( $\Delta H^\ddagger = 15.3$  kcal.,  $\Delta S^\ddagger = -23$  e.u. in chlorobenzene) with formation of *tert*-butyl alcohol and carbon dioxide. The rate of this reaction at 90° in twenty nonhydroxylic solvents varies by a factor of 140 and is related to the dielectric constants and to the polarizabilities of the solvents. The solvent effects are closely related to those found in ionic reactions of amines with alkyl halides and are similar to the solvent effects found in other polar transformations.

The formation of ion pairs by heterolytic breakage of the oxygen-oxygen bond of some organic peroxides is well established. For example,<sup>1</sup> the decomposition of 9-decalylperoxy benzoate occurs more readily in polar solvents such as nitromethane or acetonitrile than in nonpolar solvents like benzene or carbon tetrachloride. The rates in hydroxylic solvent mixtures<sup>2,3</sup> and in some nonhydroxylic solvents<sup>4</sup> follow empirical measures of solvent effects which indicate the formation of ionic states. The polarity of the transition state is shown when electron-withdrawing substituents on the aromatic ring of this peroxy ester increase the rate of decomposition.<sup>5,6</sup> Similar solvent and substituent effects indicate the formation of ionic states in the unimolecular decomposition of *tert*-butylperoxy sulfonates,<sup>2,3</sup> substituted dibenzoyl peroxides,<sup>7</sup> and some *tert*-butylperoxy esters.<sup>8</sup>

A bimolecular base-catalyzed decomposition of certain peroxide compounds<sup>9</sup> also appears to be an ionic reaction. As noted by Kornblum and De La Mare,<sup>10</sup> compounds where a hydrogen atom is attached to the carbon bearing the peroxy group may undergo base-catalyzed decomposition to yield carbonyl compounds. They suggested the following steps for the reaction.

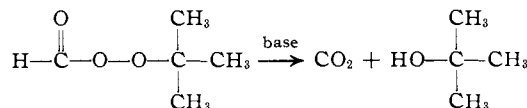


The atom attacked by the base was demonstrated by a kinetic isotope effect when deuterium was substituted for hydrogen in reaction of 1-phenylethyl *tert*-butyl peroxide with base.<sup>11</sup> The suggestion of a polar transition state in this type of bimolecular cleavage of an oxygen-oxygen bond was supported by Bell and McDougall<sup>12</sup> who showed that the reaction of benzyl

*tert*-butyl peroxide with triethylamine in chlorobenzene has a negative entropy of activation consistent with a highly polar transition state formed from two uncharged molecules. In this type of base-catalyzed elimination reaction the formation of an ionic transition state might be expected to be forced by the electron-donating property of the attacking base. This would be similar to the polarizing effect of internal substituents in the ionic decompositions of decalylperoxy benzoate<sup>5,6</sup> or some substituted benzoyl peroxides.<sup>7</sup>

A reaction which shows such ionic character in a solvent like chlorobenzene is interesting with regard to the question of the effects of nonpolar solvents on ionic reactions. Most studies of solvent effects on reactions yielding ions or ion pairs have been concerned with solvolysis reactions in which only more ionizing solvents such as alcohols, acids, and mixtures of water with nonpolar solvents are used.<sup>13</sup> There is difficulty in generating ions in nonpolar nonhydroxylic solvents<sup>14</sup> and complications arise from autocatalytic effects,<sup>4</sup> and from insolubility and precipitation of reaction products.<sup>15</sup> These have generally restricted studies of ionization processes in such solvents.

To investigate the ionic character of the bimolecular catalyzed decomposition of peroxides and to study the effects of solvents on this potentially dipolar reaction, the base-catalyzed decomposition of *tert*-butylperoxy formate has been studied in a number of solvents.



This compound<sup>16</sup> has the advantage that it is highly stable toward thermal free radical decomposition but readily undergoes decomposition in the presence of base to yield carbon dioxide and *tert*-butyl alcohol. Its great rate of pyridine-catalyzed decomposition allows the use of low concentrations of peroxide and of base so that the presence of the reactants does not change the general features of the solvent. Also, the products of the reaction are soluble and neutral so

(13) For recent studies of the ionizing power of some nonhydroxylic solvents see (a) E. J. Kosower, *J. Am. Chem. Soc.*, **80**, 3251 (1958); (b) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962), and also ref. 4.

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 139; Y. Pocker in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p. 217.

(15) N. J. T. Pickels and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936).

(16) R. E. Pincock, *J. Am. Chem. Soc.*, **84**, 312 (1962).

(1) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(2) P. D. Bartlett and B. T. Story, *J. Am. Chem. Soc.*, **80**, 4954 (1958).

(3) P. D. Bartlett and T. Traylor, *ibid.*, **83**, 856 (1961).

(4) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

(5) P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953).

(6) H. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(7) J. E. Leffler and C. C. Petropoulos, *ibid.*, **72**, 67 (1950); **79**, 3068 (1957).

(8) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963).

(9) A. G. Davies, "Organic Peroxides," Butterworths and Co., London, 1961, pp. 135, 183.

(10) N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880 (1951).

(11) N. Kornblum, quoted by R. P. Bell in ref. 12; see also ref. 9.

(12) R. P. Bell and A. O. McDougall, *J. Chem. Soc.*, 1697 (1958).

difficulties due to precipitation and autocatalysis may be avoided.

### Results

**Products of Thermal and Pyridine-Catalyzed Decomposition.**—The products of decomposition of *tert*-butylperoxy formate (TBF) in degassed cumene, chlorobenzene, and chlorobenzene containing pyridine are shown in Table I.

TABLE I

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY FORMATE AT 140°

	Solvent		
	Cumene	Chlorobenzene	Chlorobenzene
Peroxide, concn., <i>M</i>	0.366	0.341	0.345
Pyridine, concn., <i>M</i>	None	None	$9.27 \times 10^{-3}$
	Products, moles per mole of peroxide		
Carbon dioxide	0.68 <sup>a</sup> .69 <sup>b</sup>	0.54 <sup>a</sup> .47 <sup>b</sup>	0.90 <sup>a</sup> .90 <sup>b</sup>
Methane <sup>c</sup>	.20	.19	.02
Formic acid	.14	.25	.02
<i>tert</i> -Butyl alcohol	.88	.25	.90
Acetone	.18	.53	.05
Nonvolatile residue	(.60 g.) <sup>d</sup>	(.20 g.) <sup>e</sup>	(.042 g.)

<sup>a</sup> By volumetric analysis. <sup>b</sup> By absorption on Ascarite. <sup>c</sup> Mass spectrometric analysis indicated predominantly methane. <sup>d</sup> Predominantly dicumyl as identified by infrared spectrum and melting point. <sup>e</sup> Showed carbonyl absorption at 5.8  $\mu$ .

The thermal decomposition of TBF at 140° in cumene and chlorobenzene gives rise to carbon dioxide, formic acid, *tert*-butyl alcohol, acetone, methane, and non-volatile material derived from the solvent. No hydrogen was present in the product gases. These products are indicative of formyloxy and *tert*-butoxy radicals formed by the simple cleavage of the peroxide bond. The greater ratio of *tert*-butyl alcohol to acetone found in cumene reflects the greater ease of hydrogen atom donation by this solvent.

The presence of only 2.6% pyridine relative to peroxide changes the products in chlorobenzene to essentially carbon dioxide and *tert*-butyl alcohol and almost completely prevents the formation of products of the uncatalyzed thermal decomposition. Triethylamine is a more effective catalyst and even solid sodium carbonate decomposes the performate to carbon dioxide and *tert*-butyl alcohol at room temperature.

**Kinetics of Thermal and Catalyzed Decompositions at 140°.**—The decomposition of TBF in various degassed solvents was followed by measuring the loss of its intense carbonyl absorption at 1760  $\text{cm}^{-1}$ . The data for runs in chlorobenzene, chlorobenzene with added styrene, cumene, and *p*-chlorotoluene are given in Table II. The rate of decomposition was first order in peroxide with no evidence of a higher order reaction in chlorobenzene when the peroxide concentration was increased by a factor of five. The rates of decomposition in the three solvents and in chlorobenzene containing styrene are the same, as expected for first-order thermal decomposition which yields free radicals.<sup>17</sup>

(17) The rate constant in cumene is not larger than in the other solvents and induced decomposition does not occur in cumene, contrary to the previous report.<sup>16</sup> The earlier rates were measured in a solvent apparently containing a trace of base impurity which accelerated the rate. The suspected impurity probably was carried over during distillation of the solvent from sodium. It would presumably be a very strong base and therefore very effective at low concentrations. See discussion of induced decomposition and Experimental section.

TABLE II

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY FORMATE

Solvent	Peroxide concn., <i>M</i>	Temp., °C.	$k \times 10^4$ , $\text{sec}^{-1}$
Chlorobenzene	0.0274	140.8	1.62
	.0260	140.8	1.67
	.135	140.8	1.71
	.0257	140.6	1.79
	.0249	130.8	0.571
	.0243	130.8	.548
Chlorobenzene with styrene	.138	130.8	.538
	0.1 <i>M</i> styrene	0.0280	140.6
0.4 <i>M</i>	.0280	140.6	1.58
0.8 <i>M</i>	.0280	140.6	1.62
1.6 <i>M</i>	.0280	140.6	1.80
Cumene	.0244	140.6	1.87
	.0272	140.6	1.82
	.0245	140.6	1.60
<i>p</i> -Chlorotoluene	.0257	140.6	1.61

Pyridine accelerates the decomposition of TBF but not to the same extent in all solvents. Table III contains the data for pyridine-catalyzed decomposition in chlorobenzene, cumene, and *p*-chlorotoluene at 140°. This catalyzed decomposition is first order in TBF and follows the rate law

$$-d[\text{TBF}]/dt = k_1[\text{TBF}] + k_2[\text{TBF}][\text{base}]$$

where the observed rate constant is equal to  $k_1 + k_2[\text{base}]$  as shown in Fig. 1. This plot of observed

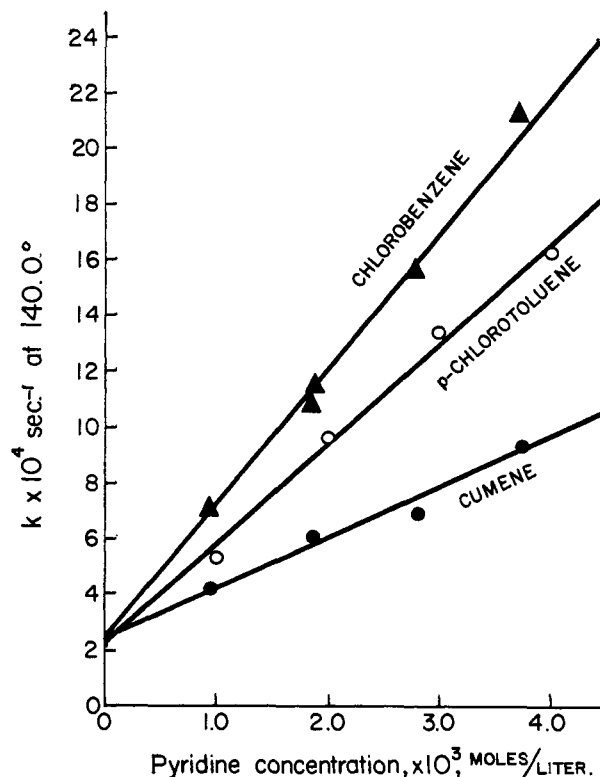


Fig. 1.—Effect of pyridine concentration on observed first-order rate constant at 140° for decomposition of *tert*-butylperoxy formate in chlorobenzene, *p*-chlorotoluene, and cumene.

first-order rate constant against pyridine concentration extrapolated to zero pyridine concentration gives essentially the same value of  $k_1$  ( $\text{ca. } 2.2 \times 10^{-4} \text{ sec}^{-1}$ ) for the three solvents. This compares with the average value obtained by uncatalyzed decomposition

in these solvents of  $1.7 \times 10^{-4}$  sec.<sup>-1</sup>. Within the limits of accuracy of the measured rate constants and the extrapolation method, the unimolecular decomposition of the peroxide is not sensitive to solvent. However, the different slopes of Fig. 1 for the three solvents show that the bimolecular decomposition is solvent sensitive. The second-order rate constant in chlorobenzene is 0.51 l. mole<sup>-1</sup> sec.<sup>-1</sup> and is about one-half as great in cumene.

TABLE III

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY FORMATE CATALYZED BY PYRIDINE AND BY ACETIC ACID AT 140°

Solvent	Peroxide concn., <i>M</i>	Pyridine concn. $\times 10^2$ , <i>M</i>	$k_{\text{obsd}} \times 10^4$ , sec. <sup>-1</sup>	
Chlorobenzene	0.0280	None	1.86	
	.0268	0.925	7.04	
	.135	1.85	8.79	
	.0268	1.85	10.8	
	.0209	1.88	11.5	
	.0265	2.78	15.6	
	.0268	3.70	21.2	
	.0265 <sup>a</sup>	3.70	18.0 <sup>a</sup>	
	.0265 <sup>b</sup>	3.70	18.1 <sup>b</sup>	
	.0256	0.93	4.30	
	.0270	1.86	6.10	
	.0256	2.79	6.93	
	.0256	3.72	9.39	
Cumene	.0251 <sup>a</sup>	3.72	10.0 <sup>a</sup>	
	.0251 <sup>b</sup>	3.72	10.4 <sup>b</sup>	
	.0226	0.995	5.34	
	.0223	1.99	9.63	
	.0226	2.98	13.4	
<i>p</i> -Chlorotoluene	.0226	3.98	16.2	
	Acetic acid concn. $\times 10^3$ , <i>M</i>			
	Chlorobenzene	0.0248	5.82	2.53
		.0253	11.6	3.04
	.0257	23.4	3.19	
	.0248	40.8	5.06	

<sup>a</sup> Solvent contains 0.6 *M* quinone. <sup>b</sup> Solvent contains 0.18 *M* styrene.

As shown in Table III the presence of styrene or quinone does not inhibit the base-catalyzed decomposition nor greatly change the rate of decomposition. The rate of decomposition of TBF in chlorobenzene is increased by addition of acetic acid (see Table III), but the effect is small relative to the pyridine-catalyzed decomposition and the increase in observed rate constant is not proportional to the concentration of acetic acid.

**Effect of Various Solvents on the Pyridine-Catalyzed Decomposition.**—To study the variation of the second-order rate constant,  $k_2$ , in different solvents it was convenient to measure rates at 90° instead of 140°. The base-catalyzed decomposition may be studied at this lower temperature without the complication of a concurrent first-order decomposition (which has a calculated half-life of 400 hr. at 90°). At 90° the runs were always pseudo first order in peroxide, at any concentration of base. The second-order rate constants were obtained by dividing the observed rate constant by the base concentration of the run. Table IV contains the second-order rate constants for pyridine-catalyzed decomposition of TBF at 90° in various solvents. These values are the average of usually three runs at concentrations of peroxide from 0.02 to 0.035 *M* and a variation of pyridine concentration by a

factor of about two to five in each solvent. The range of pyridine concentration was from 0.10 *M* in heptane to  $8 \times 10^{-3}$  *M* in nitrobenzene. These concentrations were low enough so that the calculated second-order rate constants showed no noticeable dependency on pyridine concentration (see Experimental).

TABLE IV

RATES OF PYRIDINE-CATALYZED DECOMPOSITION OF *tert*-BUTYLPEROXY FORMATE IN VARIOUS SOLVENTS AT 90°

Solvent	$k_2 \times 10^3$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	Solvent	$k_2 \times 10^3$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
Nitrobenzene	212 ± 13 <sup>a</sup>	Benzene	21.5 ± 1.4 <sup>a</sup>
Nitromethane	167 ± 5	Toluene	17.7 ± 0.7
Dichloromethane <sup>b</sup>	69.0 ± 1.4	Cumene	15.1 ± .8
Chloroform <sup>b</sup>	45.2 ± 0.7	<i>p</i> -Xylene	13.7 ± .5
Chlorobenzene	40.9 ± .4	<i>p</i> -Cymene	11.7 ± .3
<i>p</i> -Chlorotoluene	39.7 ± .4	<i>n</i> -Butyl ether <sup>d</sup>	7.01 ± .2
Diphenylmethane	37.1 ± 2.4	CCl <sub>4</sub> <sup>b</sup>	6.08 ± .1
Styrene	33.0 ± 0.8	Cyclohexene	3.79 ± .12
Tetrahydrofuran <sup>c</sup>	30.8 ± 1.2	Cyclohexane	2.11 ± .15
Dioxane <sup>c</sup>	23.0 ± 0.8	Heptane	1.52 ± .12

<sup>a</sup> Average deviation of rate constant in several runs. <sup>b</sup> Samples of kinetic runs were degassed. <sup>c</sup> Containing 0.01 to 0.135 *M* quinone to inhibit radical reactions. <sup>d</sup> The oxygen present was shown to be sufficient to inhibit any radical reactions.

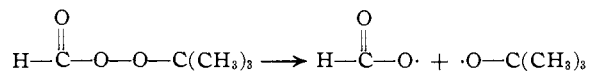
As indicated by qualitative infrared analysis, the products of the pyridine-catalyzed decomposition in the solvents listed in Table IV were carbon dioxide and *tert*-butyl alcohol.

**Decomposition in Ether Solvents.**—*tert*-Butylperoxy formate in degassed *n*-butyl ether at 90° decomposes with first-order kinetics. The rate corresponds to half-lives of 82 min. for a 0.032 *M* solution, 74 min. for a 0.374 *M* solution. This rate is three hundred times faster than that calculated for the thermal decomposition in chlorobenzene at this temperature. Only 18% carbon dioxide is formed from decomposition of the peroxide (0.34 *M*) in degassed *n*-butyl ether at 90° while 42% more of the formate group is accounted for as formic acid. The decomposition is inhibited by oxygen since a 0.03 *M* solution was only 7% decomposed after 180 min. in nondegassed *n*-butyl ether. The decomposition in tetrahydrofuran or dioxane was faster than in *n*-butyl ether. A 0.02 *M* solution in degassed tetrahydrofuran was half decomposed in 12 min. at 90°. Quinone was an effective inhibitor of this induced decomposition and was used to allow study of the pyridine-catalyzed decomposition in these solvents. Variation of the concentration of quinone from 0.013 to 0.135 *M* in dioxane did not affect the rate of base-catalyzed decomposition.

### Discussion

**Free Radical Decomposition.**—As established by Bartlett and Hiatt,<sup>18</sup> the thermal decomposition of *tert*-butylperoxy esters occurs with direct formation of an alkyl radical, carbon dioxide, and a *tert*-butoxy radical provided the alkyl radical is more stable than a simple primary or phenyl radical. The simultaneous formation of carbon dioxide accelerates the decomposition over that of *tert*-butylperoxy acetate where only the oxygen-oxygen bond is broken in the rate-determining step.<sup>18</sup> The slow rate of decomposition of *tert*-butylperoxy formate, which is one-half as great as that of *tert*-butylperoxy acetate, shows that homo-

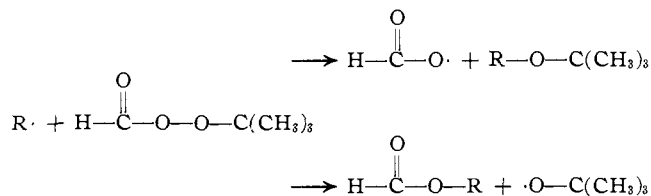
lytic cleavage of only the peroxide bond occurs in the initial step of decomposition. The rate of this unimolecular reaction involving the formation of free radicals does not noticeably vary with solvent<sup>19</sup> nor is it affected by the inhibitor styrene (see Table II).



The greater stability of the performate compared to *tert*-butylperoxy acetate is consistent with the stabilizing effect on peroxide bonds of electron-withdrawing groups as found in the free radical decompositions of substituted phenyl peroxyacetates,<sup>20</sup> peroxybenzoates,<sup>21</sup> and benzoyl peroxides.<sup>22,23</sup> In these cases the peroxide derived from the stronger acid is more stable, so *tert*-butyl peroxyformate is more stable than *tert*-butyl peroxyacetate.

The products of thermal decomposition in cumene or chlorobenzene (Table I) also indicate that simple peroxide bond cleavage is the only process in the initial step of decomposition. Formation of carbon dioxide would not necessarily occur by decarboxylation of formyloxy radicals with formation of a free hydrogen atom. This would probably require an even greater activation energy than decarboxylation of acetoxy radicals since the formate carbon-hydrogen bond is stronger than the acetate carbon-carbon bond. The formation of carbon dioxide may occur by a disproportionation reaction of formyloxy radical with other radicals such as *tert*-butoxy radical. This is similar to the suggested reaction for formation of carbon dioxide from two acetoxy radicals.<sup>24</sup>

The decomposition of TBF in ether solvents occurs by a free radical-induced mechanism as shown by the accelerated rates, relative to that calculated for thermal decomposition, and by the inhibition of the decomposition by quinone or oxygen. The formation of little carbon dioxide and a relatively greater amount of formic acid indicate that the position of attack by radicals on the peroxide is one or more of the oxygen atoms of TBF and not on the formate hydrogen.<sup>16,17</sup> A chain step similar to that found for the induced decomposition of benzoyl peroxide<sup>25-27</sup> accounts for these products.



The kinetic order for decomposition of TBF in *n*-butyl ether, first order in peroxide, is also similar to that of benzoyl peroxide in *n*-butyl ether<sup>27</sup> and similar chain

(19) The rate of free radical decomposition of simple peroxy esters is not solvent sensitive.<sup>8,20</sup> However, neighboring group effects in decomposition of *tert*-butylperoxy *o*-phenylthiobenzoate result in a free radical reaction whose rate varies greatly with solvent. See D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963).

(20) P. D. Bartlett and C. Ruchardt, *ibid.*, **82**, 1756 (1960).

(21) A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

(22) C. G. Swain, W. H. Stockmeyer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(23) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

(24) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(25) D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959).

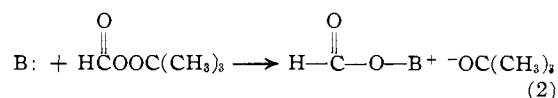
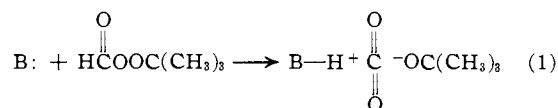
(26) J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961).

(27) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

steps and termination steps are indicated for these peroxides.

**Base-Catalyzed Decomposition.**—In contrast to the high thermal stability of TBF, this peroxide readily decomposes to *tert*-butyl alcohol and carbon dioxide when catalyzed by low concentrations of base. This affect cannot be to generate radicals by reaction of peroxide with base<sup>28</sup> and thereby promote an induced chain decomposition since the rate of reaction and the formation of products are unaffected by inhibitors such as oxygen, styrene, and quinone. Nor is a free radical reaction indicated by the nature of the products. If formyloxy radical were present, formic acid would arise in the products and if *tert*-butoxy radical were present considerable acetone rather than *tert*-butyl alcohol would be formed. The acetone-*tert*-butyl alcohol ratio has been used as an indication of ionic or radical intermediates in decompositions of *tert*-butylperoxy esters.<sup>8,19</sup>

The products and the second-order kinetics, first order in peroxide and in base, are accounted for by a direct nonradical reaction of base with peroxide. Of the several possible points of attack by base on the peroxide, those reasonably leading to *tert*-butyl alcohol and carbon dioxide involve bond formation with the formate hydrogen (eq. 1) or bond formation with one of the peroxide oxygens (eq. 2). Subsequent transfer of a proton to *tert*-butoxide ion would give *tert*-butyl



alcohol and carbon dioxide while regenerating the base. Equation 1 is a reaction as proposed in general by Kornblum and De La Mare<sup>10</sup> while eq. 2 is similar to the mechanism proposed by Walling<sup>28,29</sup> for reaction of benzoyl peroxide with nitrogen bases. The more direct formation of carbon dioxide and *tert*-butyl alcohol through nucleophilic attack on the formate hydrogen (eq. 1) seems to be supported by several types of evidence. This mechanism applies in base-catalyzed reaction of 1-phenylethyl *tert*-butyl peroxide as shown by the observed large deuterium isotope effect.<sup>11</sup> In similar compounds where hydrogen is adjacent to the peroxide group the carbonyl-forming elimination reaction competes easily with nucleophilic attack directly on oxygen.<sup>9</sup> The reaction of pyridine with *tert*-butylperoxy acetate is much slower than the reaction of pyridine with TBF, suggesting that the performate has a decomposition path which is not available to the peracetate. Also the fact that reaction of TBF with triethylamine is some twenty thousand times faster than that of benzyl *tert*-butyl peroxide with triethylamine in chlorobenzene at 80<sup>o</sup><sup>12</sup> does not appear reasonable by a mechanism for these two carbonyl-forming reactions which involves attack at oxygen. The accelerated rate of TBF is accounted for in a reaction involving attack on hydrogen when carbon dioxide is

(28) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 590.

(29) C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958).

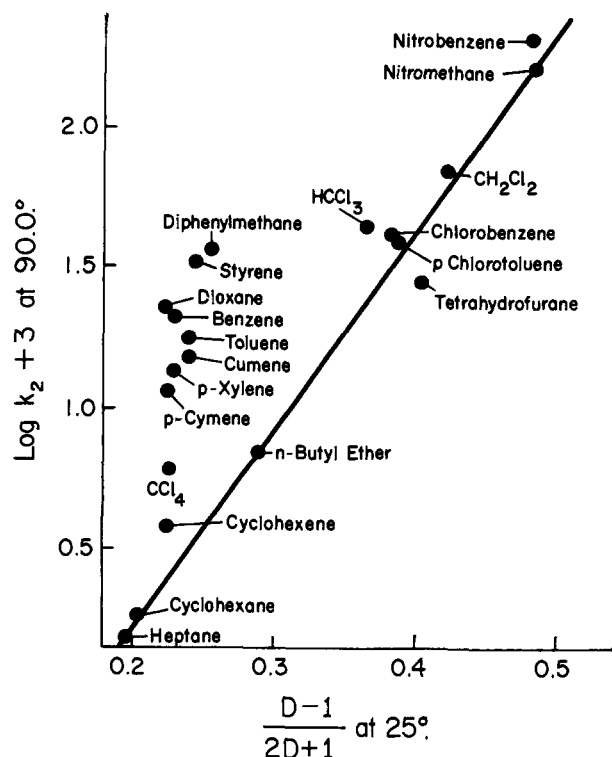
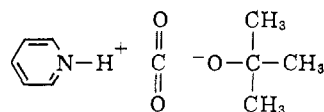


Fig. 2.—Plot of  $\log k_2$  for pyridine-catalyzed decomposition of *tert*-butylperoxy formate at  $90^\circ$  against a function of dielectric constant (ref. 31, 32). Dielectric constants taken at  $25^\circ$  from A. A. Maryott and E. R. Smith, "Tables of Dielectric Constants of Pure Liquids," National Bureau of Standards Circ. No. 514 (1951).

formed in the initial step. This contributes to lowering the required activation energy similar to the observed effect in concerted formation of carbon dioxide during the thermal decomposition of most peroxy esters.<sup>18</sup>

**Solvent Effects.**—The first-order rate of thermal decomposition of TBF, as with other simple peroxy esters,<sup>19</sup> is not sensitive to solvent changes. However, solvent effects vary the rate of pyridine-catalyzed decomposition by a factor of one hundred and forty from heptane to nitrobenzene. As shown in Table IV the more polar solvents like nitrobenzene and nitromethane are the "faster" solvents while nonpolar solvents like heptane or cyclohexane are "slower." Such changes in rate with solvent indicate a reaction in which a dipolar transition state is formed from relatively nonpolar initial states. The pyridine-catalyzed decomposition of this peroxide, if an extreme displacement of charge occurred, would lead to the generation of pyridinium ion and *tert*-butoxide ion separated initially by a carbon dioxide molecule. This reaction,



just like unimolecular ionic decompositions of peroxides or other ionization processes, should then be accelerated by more ionizing solvents and should show other characteristics of ionic reactions.<sup>30</sup> Many of

(30) The activation parameters for thermal free radical decomposition of TBF in chlorobenzene are  $\Delta H^\ddagger = 38$  kcal.,  $\Delta S^\ddagger = 15$  e.u. For pyridine-catalyzed decomposition in chlorobenzene  $\Delta H^\ddagger = 15.3$  kcal.,  $\Delta S^\ddagger = -23$  e.u. This is consistent with a bimolecular ionic reaction for the catalyzed decomposition which involves considerable orientation of solvent by the polar

the changes in rate with solvent listed in Table IV may be explained in a qualitative way on this basis. However, a quantitative correlation of the rates with the bulk dielectric constants of the solvents is not obtained. Figure 2 presents the solvent effect data of Table IV in terms of a function of dielectric constant of the solvent as suggested by the Kirkwood equation.<sup>31,32</sup> A general increase in rate with dielectric constant is shown. For example, carbon tetrachloride, chloroform, and dichloromethane are structurally similar solvents with different dielectric constants which show rate differences paralleling the rate change from heptane of lowest dielectric constant to nitrobenzene of highest dielectric constant. But changes in rate occur among solvents which differ little in either dielectric constant or in general structure. Thus, the rate in cyclohexene is greater than in cyclohexane, in diphenylmethane greater than in benzene, and in benzene greater than in *p*-cymene. Although the common lack of correlation of rates of ionic reactions with the bulk dielectric constant of solvents is well known,<sup>33</sup> presentation of the data according to the function of dielectric constant serves to point out that relatively great changes of rate may occur in solvents which differ little in their dielectric constants. The change in rate from heptane ( $D$  1.92) to benzene ( $D$  2.28) is greater than the change from benzene to nitrobenzene ( $D$  34.8), and solvents with very low dielectric constants vary greatly in their ability to aid this ionic decomposition.

As a general class all the aromatic compounds are more effective solvents than expected from their dielectric constants. This has been noted in other dipolar reactions such as the reaction of amines with alkyl halides to form quaternary ammonium salts and has been ascribed to the greater polarizability of aromatic  $\pi$ -electrons.<sup>34</sup> Since neither benzene nor heptane have a permanent dipole moment, the ratio of fourteen in the rates in these solvents seems reasonable on the basis of a polarizability effect. Polarizability as a factor in solvent effects on dipolar reactions<sup>35b</sup> and electronic transitions<sup>35-38</sup> has been treated in terms of the refractive index of the solvents. As the refractive index is a measure of polarization induced by the magnetic field of light and similar polarization is induced by the electric field of a dipole, then some relationship between relative ease of formation of a dipole (*i.e.*,  $\log k_2$ ) and refractive index may be expected. The relationship derived from electrostatics for the energy of interaction of a dipole with an induced dipole indicates the energy is proportional to the polarizability of the induced dipole.<sup>39</sup> The polariz-

transition state.<sup>12</sup> Also, the rate of pyridine-catalyzed decomposition of TBF in acetonitrile at  $70^\circ$  is doubled by 0.1 *M* anhydrous lithium perchlorate.

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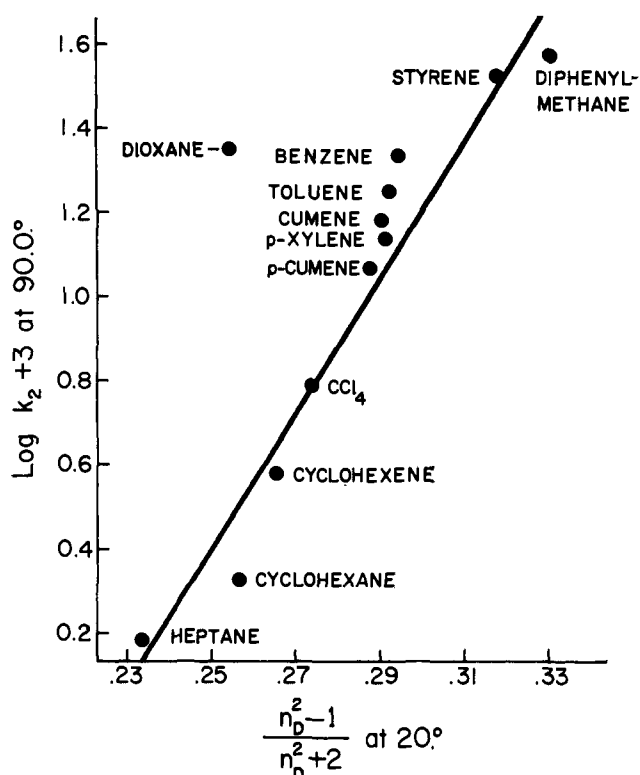


Fig. 3.—Plot of  $\log k_2$  for pyridine-catalyzed decomposition of *tert*-butylperoxy formate at  $90^\circ$  in solvents with little or no dipole moment against polarizability per unit volume at  $20^\circ$ . Values of refractive index were taken from A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955.

ability per unit volume of a medium is obtained by the Lorentz-Lorenz equation as  $(n^2 - 1)/(n^2 + 2)$  where  $n$  is refractive index.<sup>40</sup> Figure 3 shows  $\log k_2$  against this measure of polarizability for solvents which contain little or no permanent dipole moment. Except for dioxane a rough relationship is indicated and induced polarization is supported as an important factor in solvents of low dielectric constant. All the other solvents studied have a relatively large permanent dipole and give rates greater than expected from their refractive index. The points corresponding to rates in these solvents are not included in Fig. 3 since orientation of permanent dipoles is not measured by refractive index.<sup>40,41</sup> For example, *n*-butyl ether and tetrahydrofuran give rates greater than would be expected from their polarizabilities and the relationship of other solvents in Fig. 3. Dioxane is unusual in that it has greater ability to aid polar transformations than expected from either its low refractive index or low dielectric constant.<sup>37,38,42,43</sup> As shown in Fig. 3, the aromatic solvents have no unique ability to aid ionization reactions, other than they have high polariz-

(40) This function of refractive index, using refractive index at the sodium  $D$  line at  $20^\circ$ , is chosen for its simplicity and direct relation to molar polarizability. Other functions<sup>38-39</sup> have been used as measures of polarizability and these give the same rough relation with rate as shown in Fig. 3. For molecules without permanent dipoles the square of refractive index is equal to the dielectric constant, so Fig. 2 and 3 do not show independent treatments of the solvent effects. However, the refractive index is a better measure of induced polarization since the dielectric constant contains both induced polarization and orientation polarization terms.<sup>41</sup>

(41) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 13, 403.

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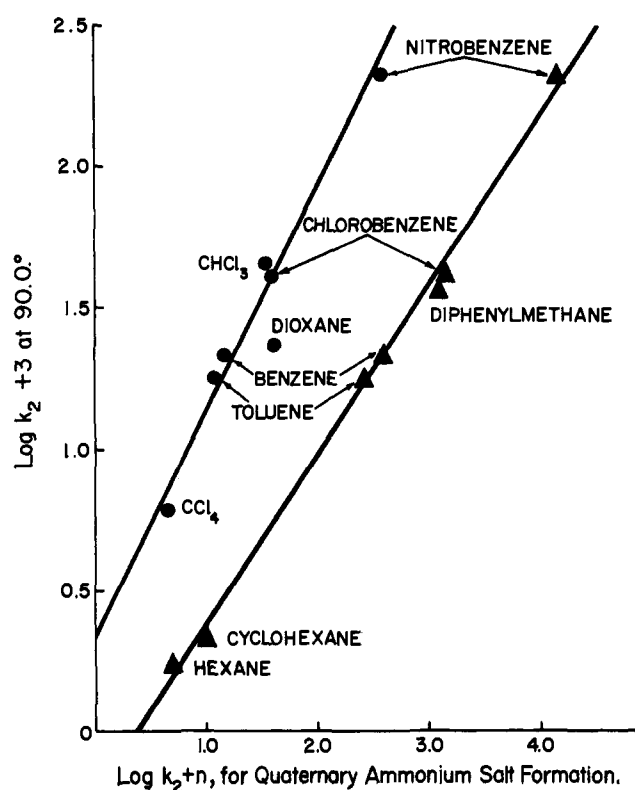


Fig. 4.—Relation of solvent effects in ionic decomposition of *tert*-butylperoxy formate at  $90^\circ$  to those in formation of quaternary ammonium salts: ●, reaction of pyridine with methylamine at  $100^\circ$ ,  $n = 4$  (ref. 15); ▲, reaction of triethylamine with ethyl iodide at  $100^\circ$ ,  $n = 6$  (ref. 45).

abilities, since carbon tetrachloride and even cyclohexene are about as effective as expected from their polarizabilities.

The solvents in this study seem to divide into two groups; those with large permanent dipoles which give rates roughly expected from their dielectric constants and those with little or no dipole moment which give rates roughly expected from their polarizabilities. The polarizability factor appears to give rise to as great a rate difference as the dielectric constant factor.

Although there are some qualitative relationships between the rate of this reaction and simple macroscopic solvent properties, it is more reasonable to expect in general<sup>44</sup> that dipolar reactions would respond similarly to solvent changes even though the response cannot be quantitatively predicted from specific solvent properties. This is the basic reason for the success of the empirical solvent parameters<sup>44</sup>  $Y$ ,  $Z$ ,<sup>13a</sup>  $\Omega$ ,<sup>13b</sup> and  $\log k_{ion}$ .<sup>4</sup> It is not yet possible to relate the solvent effects in ionic decomposition of TBF to any of these solvent parameters since they are only available for more polar solvents, hydroxylic solvents, and solvent mixtures. Still, as shown in Fig. 4, the solvent effects in the reaction of pyridine with methyl iodide<sup>15</sup> and the reaction of triethylamine with ethyl iodide<sup>45</sup> are similar to the solvent effects for TBF decomposition. Also, the solvent effects in the pyridine-catalyzed decomposition of TBF are roughly related to the solvent shift parameter  $G$  developed by Allerhand and Schleyer<sup>42</sup> for spectroscopic solvent

(44) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 169, 297, 309.

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

effects and to a similar solvent parameter suggested by Brownstein.<sup>46</sup> A highly polar reaction intermediate or transition state occurs in nonpolar solvents only when forced by instability of the initial state, as in ionic peroxide decompositions, or by the charge separation possible in a bimolecular reaction<sup>47</sup> such as formation of quaternary ammonium salts. However, since the ionic decomposition of *tert*-butylperoxy formate is subject to a large solvent effect and since the rate may be measured in a wide variety of solvents, it may serve as a basis of comparison for ionic effects in other reactions.

### Experimental

**Materials.**—Lucidol *tert*-butyl hydroperoxide was refluxed under reduced pressure in an azeotrope separation apparatus until two phases no longer separated. After a large forerun the fraction distilling at 40° (22 mm.) was collected for use.

All solvents used were reagent or spectro grade. Reagent grade solvents were dried by standard methods and distilled through a 2-ft. Vigreux column. Center fractions were collected and passed through a column of powdered type 5A Molecular Sieves and through acid-washed alumina to remove any basic impurities.

Cumene was washed several times with concentrated sulfuric acid and then with water. After drying with calcium chloride and magnesium sulfate, it was refluxed and distilled from sodium. The center fraction, b.p. 151.5°, was collected for use. An early batch of cumene prepared this way apparently contained a basic impurity which catalyzed the decomposition of *tert*-butylperoxy formate. Other solvents (*n*-butyl ether and *p*-xylene) also contained traces of basic impurities when distilled from sodium. These were removed by passing the solvent through acid-washed alumina.

Toluene, *p*-xylene, *p*-cymene, *n*-butyl ether, and cyclohexene were refluxed and distilled from sodium then passed through molecular sieves and acid-washed alumina.

Chlorobenzene was washed with concentrated sulfuric acid and then with water, dried with calcium chloride, and distilled from phosphorus pentoxide. *p*-Chlorotoluene was also distilled from phosphorus pentoxide.

Matheson Coleman and Bell styrene was distilled at reduced pressure and a center fraction collected, b.p. 49° (24 mm.).

Nitrobenzene was washed with 10% sulfuric acid and with water and then dried with calcium chloride. The center fraction, b.p. 210°, was collected for use.

Tetrahydrofuran and dioxane were purified according to Fieser.<sup>48</sup> Dioxane from a freshly opened bottle of spectro grade showed no difference in rate of decomposition of the performate.

Diphenylmethane was recrystallized twice before passage through alumina.

Nitromethane, dichloromethane, chloroform, carbon tetrachloride, benzene, cyclohexane, and heptane were spectro grade commercial materials used directly, except the ethanol present in chloroform was removed by alumina and nitromethane was passed through molecular sieves and alumina.

***tert*-Butylperoxy Formate.**—The peroxide was first prepared by reaction of *tert*-butyl hydroperoxide with excess formyl fluoride in ether at 0°. The following preparation is more convenient since acetic formic anhydride, unlike formyl fluoride,<sup>49</sup> may be easily stored under refrigeration.

To 30 g. of acetic formic anhydride (prepared from ketene and formic acid) in 100 ml. of petroleum ether (30–60°) at 0° was added a solution of 20 g. of *tert*-butyl hydroperoxide in 50 ml. of petroleum ether. The two phase mixture was rapidly stirred 18 hr. at 0°. Water was added and the organic phase washed with 150 ml. of cold water in 10-ml. portions to remove hydroperoxide and acetic acid. The organic phase was dried with magnesium sulfate, evaporated, and distilled in a short path distillation apparatus taking care to keep the pot temperature below 50°. After a small forerun, 8 to 10.8 g. (41%) of *tert*-butylperoxy formate was collected at 41–42° (22 mm.), *n*<sub>D</sub><sup>20</sup> 1.3973. This perox-

ide apparently can be safely handled at room temperature. On storage at 0° for several months it is converted to *tert*-butyl alcohol and carbon dioxide.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>: C, 50.83; H 8.53, Found: C, 51.15, 50.62; H, 8.61, 8.13.

This compound was free from *tert*-butyl hydroperoxide and *tert*-butylperoxy acetate as shown by gas-liquid chromatography (20% didecyl phthalate on firebrick at 32°) and by comparison of the infrared spectra of the authentic compounds.

**Kinetic Procedure.**—The method used in the kinetic studies was essentially that described earlier.<sup>50</sup> Analysis of the samples was carried out by measurement of the loss of carbonyl absorption at 1760 cm.<sup>-1</sup> on a Perkin-Elmer Model 21 or on a Infracord spectrophotometer using cells 0.5 mm. thick. The relative concentration at time *t* was calculated by the equation

$$P/P_0 = \frac{\log T_\infty - \log T_t}{\log T_\infty - \log T_0}$$

where *T*<sub>∞</sub> is the percentage transmission of the infinity sample viewed against pure solvent and *T*<sub>0</sub> is the percentage transmission of the first sample. In pyridine-catalyzed runs *T*<sub>∞</sub> was always zero since no compounds were formed which absorbed in the carbonyl region. Plots of log *P/P*<sub>0</sub> against time were straight lines and decomposition was usually followed to 70–80%. Rate constants were obtained from the slope of this line as calculated by the method of least squares. Second-order rate constants were then obtained by dividing through by the concentration of pyridine in the run.

Only in the case of heptane as solvent was it found that the calculated second-order rate constants depended on pyridine concentration. When the pyridine concentration was greater than about 0.2 *M* the second-order rate constant increased with increasing concentration of pyridine and was almost three times greater at 0.73 *M* than at 0.2 *M*. This is presumably an effect due to the change in the medium at high concentrations of pyridine. No integral order in pyridine was found by plotting, log *k*<sub>obs</sub> against log (pyridine concentration) from 0.1 to 0.73 *M*. The fast rate of decomposition at concentrations of pyridine greater than 0.73 *M* prevented a study of this effect over a still wider range of concentrations of pyridine in heptane at 90°. In all other solvents the rates were conveniently measurable with pyridine concentrations from about 0.01 to 0.1 *M* and a peroxide concentration of about 0.03 *M*.

**Affect of Impurities on Kinetics.**—The peroxide was stable at 90° over long periods in the purified solvents; decomposition apparently occurred only by the thermal decomposition which is very slow at this temperature. Even equivalent quantities of acetic acid (0.013 *M*) did not affect the rate of pyridine (0.013 and 0.026 *M*) catalyzed decomposition in chlorobenzene at 90° so minor acid impurities (such as formic acid or acetic acid from the method of preparation of peroxide) do not affect the rate.

The presence of oxygen did not directly affect the rate of base-catalyzed decomposition. However, if the base was present in very low concentration, it seemed to be destroyed by oxygen or products derived from oxygen under the reaction conditions. Degassing of kinetic samples for runs in chloroform, carbon tetrachloride, and dichloromethane was necessary. With triethylamine as catalyst at concentrations around 10<sup>-5</sup> *M* in chlorobenzene degassing was necessary to obtain consistent results. With oxygen present the samples were less decomposed. Such apparent inhibitory effects in nondegassed samples were previously mistaken as evidence of an induced free radical decomposition in cumene which contained some basic impurity.<sup>16,17</sup>

**Product Studies.**—Product studies were carried out in a manner previously described.<sup>60</sup> Qualitative analysis of products was by infrared spectral and gas-liquid chromatographic comparison of authentic compounds. *tert*-Butyl alcohol and acetone were quantitatively analyzed by gas-liquid chromatography; formic acid present in the product solutions was titrated with standard base. Carbon dioxide was measured by volume and by weight absorbed on Ascarite.

**Acknowledgment.**—We thank the Research Corporation for a Frederick Gardner Cottrell grant and the National Research Council of Canada for support of this work.

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