



**Table I.** Decomposition of *t*-Butylperoxy Formate by 2,6-Lutidine in Frozen *p*-Xylene Solutions

Run	Concn. TBF, $M \times 10^2$	Concn. base, $M \times 10^2$	Temp., °C.	$k_{\text{obsd.}} \times 10^6$ sec. <sup>-1</sup>
1 <sup>a</sup>	2.92	1.12	0.0	46.2
2 <sup>b</sup>	2.92	1.12	0.0	50.2
3 <sup>c</sup>	2.57	0.0386	0.0	2.69
4 <sup>d</sup>	2.88	0.0773	0.0	4.82
5	3.08	1.16	11.0	8.56
6	3.08	1.19	6.0	33.5
7	3.08	1.19	2.0	52.4
8	3.05	1.16	-10.0	36.1
9	3.09	1.25	-20.0	19.3
10	3.05	1.16	-30.0	7.61
11 <sup>e</sup>	3.0	1.2	0.0	0.23
12	3.05	2.06	0.0	62.4
13	3.05	4.98	0.0	77.0
14	2.82	7.50	0.0	85.7
15	2.93	1.63	0.0	60.8
16	29.2	1.49	0.0	9.09
17	3.02	1.19	0.0	45.3
18 <sup>f</sup>	3.02	1.19	0.0	24.1
19 <sup>g</sup>	3.01	1.19	0.0	10.3
20 <sup>h</sup>	3.05	1.19	0.0	11.1
21 <sup>i</sup>	3.05	1.19	0.0	10.2

<sup>a</sup> Samples, ca. 2 ml., frozen slowly by seeding at +8°. <sup>b</sup> Samples, ca. 0.5 ml., frozen at -195°. <sup>c</sup> Followed to 60% decomposition. <sup>d</sup> Followed to 87% decomposition. <sup>e</sup> Calculated for reaction at the given concentration of 2,6-lutidine in *p*-xylene from  $\Delta H^* = 12.3$  kcal.,  $\Delta S^* = -30.5$  e.u., obtained for second-order rate constants measured at 90, 70, and 50°. <sup>f</sup> Solution contains 0.0149 *M* benzene. <sup>g</sup> 0.0571 *M* benzene. <sup>h</sup> 0.0473 *M* carbon tetrachloride. <sup>i</sup> 0.0368 *M* heptane.

(relative concentration) against time, followed usually to 90% decomposition. (B) Observed rate constants were independent of the method of freezing samples (see runs 1 and 2). (C) Even 2.6% 2,6-lutidine relative to the initial TBF concentration resulted in complete loss of the peroxide (runs 3 and 4). (D) The rate of reaction in frozen *p*-xylene solutions is a maximum at ca. +2° but reaction occurs at +12° and at -30° (however not at -70°) at greater rates than those calculated for the reaction in liquid at the given lutidine concentrations (see runs 5-10). (E) For constant initial peroxide concentration and low 2,6-lutidine concentrations the observed rate constants at 0° are approximately proportional to the lutidine concentration; however, at high concentrations of lutidine the observed rate constants reach a maximum (runs 3, 4, 2, 12-14). (F) Although the decomposition is first order in TBF, the observed first-order rate constants decrease with greater initial concentrations of TBF (runs 15 and 16). (G) At low concentrations of TBF and 2,6-lutidine the observed first-order rate constants are greatly sensitive to the presence of "inert" impurities (e.g., 0.16 mole % benzene in *p*-xylene decreases the observed rate by one-half; see runs 17 and 18). Within certain limits<sup>4</sup> the nature of the impurity is unimportant; similar concentrations of different substances decrease the rate to the same extent (runs 19-21).

These results indicate that the reaction proceeds in liquid<sup>5</sup> holes, present among the crystalline solid, which

(4) Anthracene, 0.015 *M*, has no effect on the rate while *t*-butyl alcohol, 0.033 *M*, is less than half as effective in decreasing the rate as benzene, carbon tetrachloride, or heptane at the same concentration.

(5) The deuterium isotope effect for reaction of *t*-butylperoxy formate-*d* with pyridine in frozen *p*-xylene at 0° is  $k_H/k_D = \text{ca. } 9$ ,

contain high concentrations of the reactants.<sup>6</sup> If ideal behavior for the solutes is assumed then the following relationship is expected

$$k_{\text{obsd}} = k_2 C \frac{M_b}{M_b + M_p + M_i}$$

where  $k_{\text{obsd}}$  is the observed first-order rate constant,  $k_2$  is the second-order rate constant for liquid phase reaction,  $C$  is the total constant concentration of solutes in the liquid holes, and  $M_b$ ,  $M_p$ , and  $M_i$  are the initial concentrations of base, peroxide, and impurities, respectively. This relationship reproduces, from experimental measurements of  $C$  for 2,6-lutidine in *p*-xylene (i.e., from the freezing point-composition phase diagram) and from the calculated  $k_2$  extrapolated from higher temperatures, the form of the observed temperature dependence of  $k_{\text{obsd}}$  (see D above). For low and high concentrations of 2,6-lutidine or of pyridine the experimentally observed change in  $k_{\text{obsd}}$  with base concentration is correctly predicted (see E above). At high TBF concentrations or in the presence of impurities which follow ideal behavior at 0° in *p*-xylene the predicted decrease in rate constant is experimentally found (see F and G above). These variations in  $k_{\text{obsd}}$ , which are related by the above equation to measurable solution concentrations, may be visualized in terms of changes in the total volume and in the relative reactant concentrations of the liquid regions.

Many of the features reported here for the TBF-base reactions in frozen organic solutions are similar to results reported by Bruce and Butler<sup>7</sup> for several bimolecular reactions in ice. It may be generally expected that, if the reactants of a bimolecular reaction are sufficiently soluble at temperatures below the freezing point of the solvent, and the reaction has a low activation energy, an acceleration due to the concentration effect will be observed when the system is frozen. Experiments on the reaction of methyl iodide with triethylamine in benzene and the Diels-Alder reaction of cyclopentadiene with methyl acrylate in *p*-xylene at 0° show that freezing accelerates the formation of products.

close to the expected ratio for liquid phase reaction as estimated from the known isotope effects at 90°.<sup>3</sup>

(6) A concentration of 2.35 *M* 2,6-lutidine in *p*-xylene is required to prevent freezing at 0°. From this the maximum total volume of "holes" for most of the runs of Table I may be estimated to be ca. 2% of the volume of the original solution before freezing.

(7) T. C. Bruce and A. R. Butler, *J. Am. Chem. Soc.*, **86**, 313, 4104 (1964).

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### The Total Synthesis of (±)-Ibogamine and of (±)-Epiibogamine

Sir:

Ibogamine (1)<sup>1,2</sup> is the least substituted member of a large group of natural bases structurally characterized by the presence of an isoquinuclidine ring and a seven-membered ring C. We have now completed the first total synthesis of an iboga alkaloid.

(1) M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *J. Am. Chem. Soc.*, **80**, 126 (1958).

(2) G. A. Jeffrey, G. Arai, and J. Coppola, *Acta Cryst.*, **13**, 553 (1960).