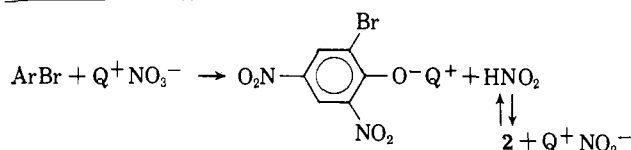
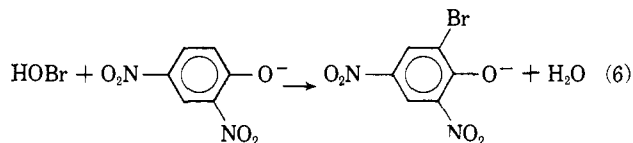
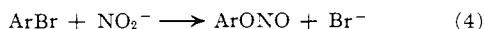


Reaction 3 is analogous to the nitrodechlorination of bromophenols known<sup>6</sup> to be effected by nitrous acid in acetic acid. This  $QNO_2$ -2 reaction was independently demonstrated (expt. 7). Kinetic data for reaction 2 (1 with  $Q(6)NO_3$  at 75°), when plotted as a second order  $NO_3^-$ -1 reaction, produced the S-shaped curve characteristic of an autocatalytic process. Addition of 10 mole % of  $QNO_2$  increased the initial rate ~75-fold, implicating  $NO_2^-$  as the autocatalyst. In view of the superior nucleophilicity of  $NO_2^-$ , the catalysis can be identified with the initial displacement of bromide,  $ArBr + NO_2^- \rightarrow ArONO + Br^-$ . An elevated oxidation state of bromine must then be sought to account for bromination of the 2,4-dinitrophenol nucleus thus generated.

This was found in the surprising power of nitrate ion to oxidize bromide in the presence of weak acid in the molten salt medium (expt. 8).<sup>7</sup> This reaction does not occur detectably in water or acetonitrile. In the  $QBr-QNO_3-ArOH$  melt it is also possible to trap bromine as stilbene dibromide. Reaction 2 can reasonably be accounted for as the sum of (4)-(7) (Ar = 2,4-dinitrophenyl).



9-Bromofluorene (1.00 mmole) fused with  $Q(5)NO_3$  (1.00 mmole) for 0.25 hr. at 105° and chromatographed on 11 g. of silicic acid gave 9-fluorenone (0.53 mmole) and 9-fluorenol (0.13 mmole) as benzene-eluted fractions. Similarly treated, *p*-nitrobenzyl bromide produced *p*-nitrobenzaldehyde (15%), *p*-nitrobenzoic acid (6%), and *p*-nitrobenzyl *p*-nitrobenzoate (26%). Molten  $Q(5)NO_3$  converted 2-bromopropane principally to propene (32%), 2-propanol (24%), and acetone (9%), with smaller amounts of 2-propyl nitrate and nitrite, 2-propyl ether, and 2-nitropropane.<sup>8</sup>

It appears that molten  $QNO_3$ , though indeed reactive, owes its reactivity not to enhanced  $NO_3^-$  nucleophilicity but to facile oxidation-reduction processes in the melt.

Further details of these reactions will be reported together with results on other systems.

(6) T. Zincke, *J. prakt. Chem.*, [2] **61**, 561 (1900).

(7) This reaction is both thermodynamically unfavorable and very slow in water; only in rather concentrated nitric acid is it observed.

(8) Sealed tube at 120-125° for 3 hr., analysis by gas chromatography; identification by retention time, confirmed by infrared and n.m.r. spectra of the product mixture.

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## The Rates of Pyridinyl Radical Reactions

Sir:

We report here the measurement of the rates of halogen abstraction by 1-ethyl-4-carbomethoxypyridinyl (1), a stable free radical,<sup>1</sup> and the conclusion that the reaction is atom transfer. This is the first report of the *direct* measurement of such a reaction, and the data allow straightforward conclusions about the transition states of the reactions.<sup>2a</sup>

Radical 1 was prepared by zinc metal reduction of the pyridinium iodide and isolated by distillation.<sup>1</sup> Solutions of 1 were treated with a large excess of dibromomethane (2), bromochloromethane (3), or dichloromethane (4) (a special apparatus permitted observation of spectral changes *in situ*). The rates were followed by means of the visible absorption band of 1. The rate of disappearance of 1 was clearly first order in all cases. The second-order constants were obtained by dividing by the concentration of halocarbon. The results are tabulated in Table I.

TABLE I  
RATES OF PYRIDINYL RADICAL REACTIONS

Radical concn., $\times 10^{-2} M$	Halocarbon concn. (M)	Solvent	Temp., °C.	$k_{obsd.}$ sec. <sup>-1</sup>	$k_2,^a$ l. mole <sup>-1</sup> sec. <sup>-1</sup>
1.20	CH <sub>2</sub> Br <sub>2</sub> (0.84)	CH <sub>3</sub> CN	25	$3.43 \times 10^{-4}$	$2.0 \times 10^{-4b}$
1.12	CH <sub>2</sub> Br <sub>2</sub> (1.30)	CH <sub>3</sub> CN	25	$5.33 \times 10^{-4}$	$2.1 \times 10^{-4b}$
0.54	CH <sub>2</sub> Br <sub>2</sub> (0.41)	CH <sub>3</sub> CN	25	$1.52 \times 10^{-4}$	$1.9 \times 10^{-4b}$
0.88	CH <sub>2</sub> Br <sub>2</sub> (0.84)	CH <sub>2</sub> Cl <sub>2</sub>	25	$1.60 \times 10^{-4}$	$1.0 \times 10^{-4b}$
1.74	CH <sub>2</sub> Br <sub>2</sub> (0.84)	<i>i</i> -PrOH	25	$0.94 \times 10^{-4c}$	$0.6 \times 10^{-4b}$
0.22	CH <sub>2</sub> Br <sub>2</sub> (1.28)	EtOH	25	$\sim 1.7 \times 10^{-4d}$	$\sim 0.7 \times 10^{-4b}$
1.13	CH <sub>2</sub> BrCl (0.84)	CH <sub>3</sub> CN	25	$8.57 \times 10^{-5}$	$1.0 \times 10^{-4}$
0.83	CH <sub>2</sub> Cl <sub>2</sub> (0.85)	CH <sub>3</sub> CN	75	$8.68 \times 10^{-6}$	$5.1 \times 10^{-6b}$
0.59	CH <sub>2</sub> Cl <sub>2</sub> (0.85)	CH <sub>3</sub> CN	50	$1.06 \times 10^{-6}$	$6.2 \times 10^{-7b}$
e	CH <sub>2</sub> Cl <sub>2</sub> (0.85)	CH <sub>3</sub> CN	25	$9.10 \times 10^{-8}$	$5.4 \times 10^{-8b}$

<sup>a</sup> Estimated reliability 5-7%. <sup>b</sup> Corrected by dividing the measured  $k_2$  by the statistical factor of 2. <sup>c</sup> Corrected for the solvent reaction with radical, with  $k_1 = 2.61 \times 10^{-5}$  sec.<sup>-1</sup> for 0.84 M CH<sub>2</sub>Cl<sub>2</sub> in isopropyl alcohol ( $Z = 75.5$ ). A solution 0.84 M CH<sub>2</sub>Br<sub>2</sub> in isopropyl alcohol has  $Z = 75.8$ . <sup>d</sup> Estimated after an approximate correction for the reaction of solvent with radical. <sup>e</sup> Extrapolated from the data at higher temperatures using  $E_a = 19$  kcal./mole. <sup>f</sup> Radical solutions in acetonitrile decrease in concentration at 75° with a half-life of 12 days.

The reaction of radical 1 with halocarbons produces 50% 1-ethyl-4-carbomethoxypyridinium halide [ $\lambda_{max}$  2740 and 2200 Å., lit.<sup>2b</sup>  $\lambda_{max}$  2735 and 2200 Å. ( $\epsilon$  4500 and 12,000), yield  $51 \pm 4\%$  in seven experiments, measured by quantitative ultraviolet spectroscopy in water at 2740 Å., silver halide formation with silver ion] and reduced pyridine derivatives [soluble in hexane, volatile, sensitive to oxygen (from 2),  $\lambda_{max}$  2420 Å. ( $\epsilon \sim 10,000$ ), reported for 1,4,4-trimethyl-1,4-dihydropyridine  $\lambda_{max}$  2708 and 2305 Å. ( $\epsilon$  3200 and 7500),<sup>3</sup> along with small amounts of polymeric material. Equation 1 summarizes these results for the reaction of 1 with 2 and includes two reasonable structures for the dihydropyridines.

The rate of the reaction of radical 1 with 2 is changed very little with a variation in solvent polarity over a wide range, from dichloromethane ( $Z = 64.2^4$ ) through

(1) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963).

(2) (a) The disproportionation of moderately stable phenoxy radicals has been reported by C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959);

(b) E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 185.

(3) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1962).

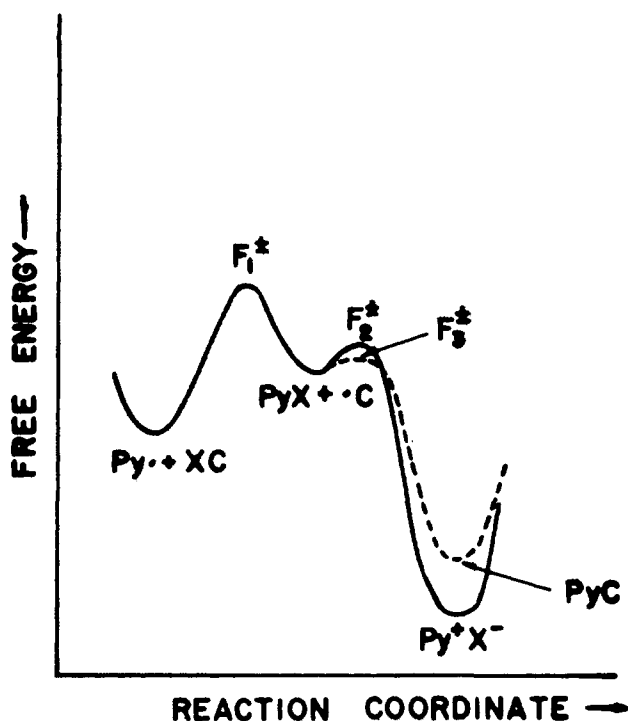
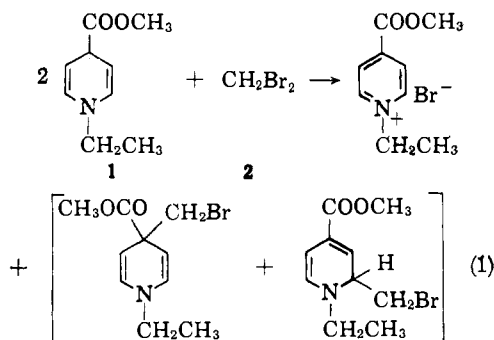
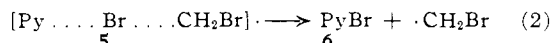


Fig. 1.—A free-energy vs. reaction coordinate diagram for halogen abstraction by pyridinyl radical. Py· is pyridinyl free radical, PyX is the adduct of halide ion and pyridinium ion,  $\text{Py}^+ \text{X}^-$  is pyridinium halide, PyC is the dihydropyridine formed from the radical,  $\cdot\text{C}$ , left by halogen abstraction and the pyridinyl radical, and  $\text{F}_1^\ddagger$ ,  $\text{F}_2^\ddagger$ , and  $\text{F}_3^\ddagger$  represent the transition-state free energies for the transformations indicated in the diagram.

acetonitrile ( $Z = 71.3$ ) and isopropyl alcohol ( $Z = 76.3$ )<sup>5</sup> to ethanol ( $Z = 79.6$ ).<sup>5</sup> The absence of a solvent effect upon the reaction rate demonstrates that the transition state for the reaction has approximately the same degree of charge separation as the initial state. The net dipole moments of the reactants,



**1** and **2**, cannot be large since both are soluble in hexane, *ca.* 0.02 *M* solutions being possible for the radical **1**. The transition state, **5**, cannot be highly charged and must decompose into the uncharged species, PyBr (**6**), the covalently bonded adduct of bromide ion, and the pyridinium ion<sup>6</sup> and a bromomethyl radical (eq. 2).



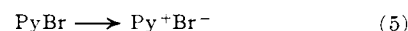
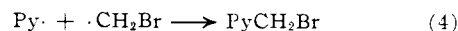
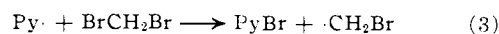
Both products disappear quickly, **6** by ionization to pyridinium bromide and  $\cdot\text{CH}_2\text{Br}$  by reaction with another molecule of **1**. The mechanism is summarized

(4) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(5) The *Z*-values of the halocarbon-alcohol mixtures are actually somewhat lower than those values cited for the pure alcohols, as noted in Table I.

(6) Cf. K. Wallenfels and H. Schüly, *Ann.*, **621**, 111 (1959).

in eq. 3, 4, and 5 and the free-energy diagram which is a necessary concomitant of these facts is shown in Fig. 1.

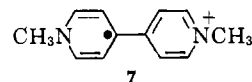


The "carbonium ion stabilization" for transition states of reactions between radicals and halocarbons or hydrocarbons proposed by Huyser,<sup>7,8</sup> Walling,<sup>9</sup> and Bamford<sup>10a</sup> cannot be significant in the case of pyridinyl radicals in spite of the fact that it would be expected that the pyridinyl radical would be unusually effective in accumulating positive charge in the transition state because of the stability of the pyridinium ion.

No spectroscopic change attributable to a charge-transfer band<sup>10b</sup> was observed for the radical **1** in dichloromethane in the visible region, although such absorption may well occur at shorter wave lengths. Visible light (irradiation with a tungsten lamp) or ultraviolet light (small amounts from the spectrophotometer) had no apparent effect on the course of the reaction. Strong ultraviolet irradiation led to a photochemical reaction with a halocarbon in one case.<sup>11</sup>

The radical **1** discriminates between different halogen-carbon bonds far more effectively than sodium<sup>12</sup> or 1-phenylethyl radicals.<sup>13</sup> It is also noteworthy that there is so little difference between chlorine and bromine with regard to stabilization of the transition state for formation of  $\cdot\text{CH}_2\text{X}$ .

Disulfides react with **1**. Less reactive pyridinyl radicals like methyl viologen cation radical (**7**) do not react appreciably with **2** at room temperature but do react with more reactive halocarbons like tetrachloro- and tetrabromomethane.<sup>13</sup>



Further studies with pyridinyl radicals are continuing and promise much fundamental information on radical reactions.

(7) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(8) E. S. Huyser, H. Schimke, and R. L. Burham, *J. Org. Chem.*, **28**, 2141 (1963).

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 158.

(10) (a) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959); (b) D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962).

(11) E. J. Poziomek, unpublished results. A photochemical reaction between **7** and ethyl iodide has been observed.

(12) J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, **36**, 465 (1940).

(13) Cf. ref. 9, p. 152.

(14) Alfred P. Sloan Fellow, 1960-1964.

(15) The authors are grateful to the National Science Foundation for financial support through Grant GP-251.

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### Metalation of Triphenylmethane by Organolithium Compounds

Sir:

The rate of metalation of triphenylmethane, *i.e.*, reaction 1, by different organolithium reagents varies