The Mechanisms of Permanganate Oxidation. VIII. Substituted Benzylamines[1]

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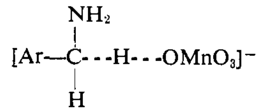
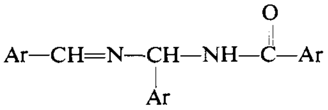
Abstract: The oxidation of benzylamine by aqueous permanganate has been shown to proceed *via* the neutral amine. A deuterium isotope effect of 7.0 at 25° has been found for benzylamine-α-d_2. In the alkaline region a second reaction whose rate is proportional to the hydroxyl ion concentration is observed. A study of 11 *meta*- and *para*-substituted benzylamines shows excellent Hammett correlation with σ^+ for 8 of the compounds, with the *p*-nitro, *m*-nitro, and *m*-trifluoromethyl derivatives deviating considerably from the Hammett plot. σ^+ was -0.28. The correlation with σ^+ and the very negative ΔS^* values obtained for the oxidation reaction suggest that the transition state is an ionic one involving extensive charge separation. The activated complex for the reaction is shown as



$$[\mathrm{Ar{-}\overset{NH_2}{\underset{H}{C}}{\cdots}H{\cdots}OMnO_3}]^-$$

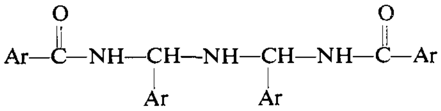
its decomposition may occur to give a radical intermediate plus manganese(VI) or an organic cation plus manganese(V). The kinetics of permanganate oxidation of benzylamines at −10° in ice was investigated from pH 7.5 to 9.3. The reaction order remains unchanged from that at 25° but the rates of oxidation are more than ten times greater in ice at −10° than in liquid water at −10°.

Benzylamine is oxidized by alkaline permanganate to give benzaldehyde, benzoic acid, and benzamide.[2] Recently, Shechter, Rawalay, and Tubis[3] made a systematic study of the products of permanganate oxidation of amines in neutral, aqueous *t*-butyl alcohol solutions. They found that using an excess of permanganate, *ortho*-, *meta*-, and *para*-substituted benzylamines are rapidly oxidized to the corresponding substituted N-[α-(benzylidineamino)benzyl]benzamides (I) and N,N′-(iminodibenzylidene)bis[benzamides] (II),



$$\mathrm{Ar{-}CH{=}N{-}\underset{Ar}{CH}{-}NH{-}\overset{O}{\overset{\|}{C}}{-}Ar}$$

I

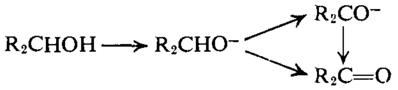


$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{Ar}{CH}{-}NH{-}\underset{Ar}{CH}{-}NH{-}\overset{O}{\overset{\|}{C}}{-}Ar}$$

II

as well as to benzoic acids and ammonia. The precise mechanism for the formation of these complex molecules was not known but it was assumed that benzalimines are the immediate products of the oxidation of benzylamines and that condensation of these imines with the parent benzylamines together with further oxidation by permanganate takes place to give I and II.

Previous studies of the mechanism of the permanganate oxidation of alcohols has revealed that the rate-controlling step is removal of hydrogen from the alkoxide ion by permanganate.[4] It has not been possible to determine whether the transferred unit is a hydride ion or a hydrogen atom, *i.e.*, whether the conversion of alkoxide ion to carbonyl compound occurs in one step or two.[5] Carbonyl compounds are produced by the alkaline permanganate oxidation of both amines and alcohols and we were interested in determining if similar mechanisms were operative. If this proved to be so we hoped that some light might be shed on the vexing problem of hydride ion *vs.* hydrogen atom transfer in permanganate oxidations.[5-8]



Experimental Section

Reagents. Benzylamine-α-d_2 was prepared from benzonitrile and lithium aluminum deuteride by the method of Halevi.[9] The infrared spectrum showed no C=N or aliphatic C—H absorption. The *m*-methyl, *m*-methoxy, and *m*-chloro derivatives of benzylamine were prepared by the lithium aluminum hydride reductions of the corresponding amides.[10]

***m*-Chlorobenzylamine.** The acetate salt had mp 81–82°. *Anal.* Calcd for $C_9H_{12}ClNO_2$: C, 53.59; H, 5.96; N, 6.95. Found: C, 53.69; H, 5.88; H, 6.87.

***m*-Methylbenzylamine.** The acetate salt had mp 92–94°. *Anal.* Calcd for $C_{10}H_{15}NO_2$: N, 7.73. Found: N, 7.65.

***m*-Methoxybenzylamine.** Hydrochloride salt had mp 141–142° (lit.[11] mp 165.5–166.5°). *Anal.* Calcd for $C_8H_{12}ClNO$: N, 8.07. Found: N, 8.16. The acetate salt had mp 94–96°. *Anal.* Calcd for $C_{10}H_{15}NO_3$: N, 7.11; H, 7.62; C, 60.90. Found: N, 7.02; H, 7.89; C, 60.92.

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(1) From the Ph.D. Thesis of M.-M. Wei, University of British Columbia, 1965. The financial support of the National Research Council of Canada is gratefully acknowledged.

(2) K. Kindler, *Ann.*, 43, 187 (1923).

(3) H. Shechter, S. S. Rawalay, and M. Tubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964); H. Shechter and S. S. Rawalay, *ibid.*, **86**, 1706 (1964).

(4) R. Stewart, *ibid.*, 79, 3057 (1957); R. Stewart and R. Van der Linden, *Discussions Faraday Soc.*, 211 (1960).

(5) R. Stewart, "Oxidation Mechanisms: Applications to Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 63–67.

(6) R. Stewart in "Oxidation in Organic Chemistry" Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965 pp 49, 50.

(7) J. L. Kurz, *J. Am. Chem. Soc.*, **86**, 2229 (1964).

(8) K. B. Wiberg and A. S. Fox, *ibid.*, **85**, 3487 (1963).

(9) E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

(10) V. M. Micovic and M. L. T. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(11) M. G. Ettlinger, and A. J. Lundeen, *J. Am. Chem. Soc.*, **78**, 1952 (1956).

The *p*-nitro, *m*-trifluoro, *m*-nitro, and *p*-ethyl derivatives of benzylamine were prepared by a modified Sommelet procedure.[12] The acetate salts were made by addition of glacial acetic acid to an ethereal solution of the amines; the resulting salts were then sublimed twice.

***p*-Nitrobenzylamine.** The acetate salt had mp 145–147°. *Anal.* Calcd for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.66; N, 13.21. Found: C, 50.75; H, 5.91; N, 13.20. The hydrochloride salt had mp 252° dec (lit.[13] mp 250°). The sulfate salt had mp 219–220° (lit.[14] mp 232°).

***m*-Nitrobenzylamine.** The sulfate salt had mp 151–152°. *Anal.* Calcd for $C_7H_{10}N_2O_6S$: N, 11.15. Found: N, 10.80.

***p*-Ethylbenzylamine.** The hydrochloride salt had mp 202–205° dec. *Anal.* Calcd for $C_9H_{14}ClN$: Cl, 20.7. Found: Cl, 20.3.

***m*-Trifluoromethylbenzylamine.** The following analysis was obtained. Calcd for $C_8H_8F_3N$: C, 54.83; H, 4.62; N, 8.00. Found: C, 54.94; H, 4.83; N, 8.11. Because of the anomalous oxidation rate found for this compound (see Results) further checks on the identity of *m*-trifluoromethylbenzylamine were carried out. A single, sharp peak was obtained by vapor phase chromatography. A weighed sample of the liquid amine dissolved in water to a known volume agreed with its concentration obtained by titration with standard acid to within 4%. A solution of the amine was oxidized with basic permanganate, and the intermediate, *m*-trifluoromethylbenzaldehyde, was isolated as its 2,4-dinitrophenylhydrazone derivative, mp 262° (lit.[15] mp 259–260°), yield 91.1%. Further oxidation by basic permanganate produced *m*-trifluoromethylbenzoic acid which could be recrystallized from carbon tetrachloride, mp 100–102° (lit.[16] mp 103–105.5°).

The other amines were commercially available.

Kinetic Methods. Aqueous solutions were prepared from freshly distilled amines and distilled water, which had been boiled and saturated with nitrogen in all cases except *p*-nitrobenzylamine and *m*-nitrobenzylamine. The acetate salts of these two amines were weighed and solutions were made up in volumetric flasks. The concentrations of all other amines were determined by titration with standard hydrochloric acid, using methyl red as indicator. The reaction rates were followed iodometrically as previously described.[4] For very slow reactions aliquots were delivered at the start of the reaction into stoppered volumetric flasks which were covered with aluminum foil and individually thermostated. At appropriate times the entire content of the flask was quenched and titrated as before. In other cases aliquots were withdrawn from the reaction mixture at various time intervals. From pH 2 to 10.8 the ratio of substrate to permanganate used was 3:2. This corresponds to the 3-equiv change of the substrate. It was found that from pH 11 to 11.8 this same ratio could still be used to give linear rate plots, although in this region the stoichiometric ratio of substrate to permanganate is difficult to determine since the disproportionation of any manganate that is formed is not instantaneous but is time and pH dependent. In addition the imine and aldehyde intermediates are possibly subject to oxidation by permanganate and manganate. For these reasons only initial rates up to 30% reaction were taken. Above pH 13 manganate is stable and the stoichiometric ratio of substrate to permanganate used was 1:2.

For the 3:2 ratio of substrate to permanganate, the following integrated second-order rate expression was used.[6]

$$k = \frac{1}{[\text{amine}]t} \frac{V_0 - V_t}{V_t - \frac{2}{5}V_0}$$

where V_0 = volume of thiosulfate at $t = 0$, V_t = volume of thiosulfate at time t, $^2/_5V_0$ = volume of thiosulfate at infinite time (calculated), t is in minutes, and [amine] = total amine concentration at $t = 0$. Plots of $(V_0 - V_t)/(V_t - {}^2/_5V_0)$ *vs.* time (Figure 1) gave straight lines.

Oxidations in Deuterium Oxide. Separate 25-ml stock solutions of the following compounds were prepared in water and in D_2O: potassium permanganate (0.119 g), dipotassium hydrogen phosphate (0.436 g), and benzylamine (0.122 g). The reaction mixture consisted of 10 ml of amine solution, 10 ml of phosphate buffer, 20 ml of water of D_2O, and 10 ml of potassium permanganate solution. The rate measurements were carried out at 25.0 ± 0.02° in the usual manner. The ratio of exchangeable deuterons and protons in the amine–buffer–deuterium oxide system above is 1:2800, meaning that the substrate is approximately 99.9% $PhCH_2ND_2$.

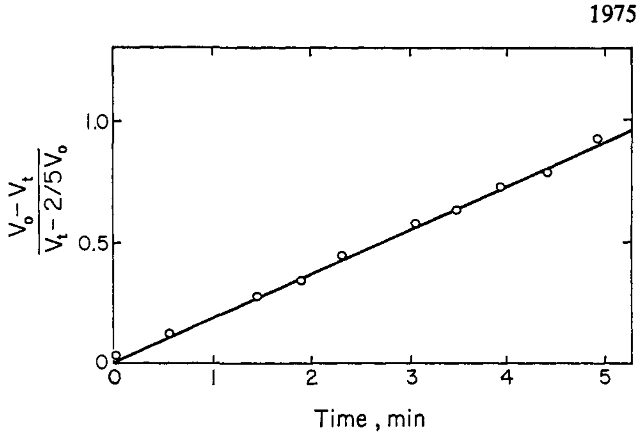

Figure 1. Second-order rate plot for the permanganate–benzylamine reaction at pH 9.90.

Product Analysis. Ammonia was formed in 93% yield by the oxidation of benzylamine at pH 10.3 as shown by partial distillation of the aqueous reaction mixture and titration of the distillate with standard base. Benzaldehyde was isolated as the 2,4-dinitrophenylhydrazone. The oxidation reaction was allowed to proceed at pH 10.4 for 16 min and then quenched with an acidic sodium bisulfite solution. After cooling in an ice bath, 15 ml of 0.04 *M* 2,4-dinitrophenylhydrazine solution was added and the mixture was stored overnight in the refrigerator. The 2,4-dinitrophenylhydrazone was filtered onto a weighed crucible, dried, and weighed. The yield was 95% of theoretical. The *m*-trifluoromethyl and N,N-dimethyl derivatives of benzylamine were converted to the 2,4-dinitrophenylhydrazones of *m*-trifluorobenzaldehyde and benzaldehyde in 91 and 95% yields, respectively.

Oxidation of Benzylamine in Ice at −10°. A typical run was carried out as follows. A pH 9.31 solution made up of 10 ml of 1 *M* buffer (K_2HPO_4), 3.94 ml of benzylamine (0.0253 *M*), 33.98 ml of water, and 2.08 ml of potassium permanganate (0.0319 *M*) was prepared in a 125-ml, red-glass flask which was cooled in an ice–water bath. Immediately after the last reagent, the permanganate, was added, a 4-ml sample was delivered into a 10-ml screw-capped bottle and immersed in a Dry Ice–acetone bath. This sample was used for the blank. Eight more samples were then prepared and were simultaneously placed undisturbed into the Dry Ice–acetone bath for 4 min. During this solidification process, the blank was warmed under hot tap water (*ca.* 50°), quenched with excess warm acidic potassium iodide solution, and transferred quantitatively into a 50-ml flask containing 10 ml of 0.3 *M* sulfuric acid. The contents was then titrated with thiosulfate solution.

After 4 min, the eight samples in the Dry Ice–acetone bath were transferred to an ice–water bath for 1 min, during which time the temperature of the samples was found to rise to approximately −10°. The samples were finally transferred to a salt–ice bath which had been adjusted to −10 ± 0.2°. The various baths were prepared in covered dewar flasks, so that temperatures were constant for the duration of the entire experiment. Initial time was taken when the samples were placed into the −10° bath. At appropriate intervals, the frozen samples were removed and warmed and analysed in the same manner as for the blank. The pH of the solutions were taken when the samples were at room temperature.

Miscellaneous Reactions. N,N-Dimethylaniline was oxidized by permanganate at pH 9.3 about eight times as fast as benzylamine whereas ammonia is oxidized very much more slowly. Permanganate failed to oxidize acetamide after 30 hr of reaction either in acidic or basic solutions. Both N,N-dimethylformamide and N-benzylformamide are slowly oxidized by permanganate at pH values higher than 13 but below this pH there is very little reaction in five or 6 hr. Whereas methylamine, dimethylamine, and trimethylamine are very rapidly oxidized by aqueous permanganate, *t*-butylamine and tetramethylammonium hydroxide exhibited no appreciable reaction after 3 or 4 hr.

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(12) J. Graymore, *J. Chem. Soc.*, 1116 (1947).

(13) H. R. Ing and R. H. F. Manske, *ibid.*, 2348 (1926).

(14) H. E. De La Mare, *J. Org. Chem.*, 25, 2114 (1960).

(15) H. Gilman, L. Tolman, F. Yeoman, L. A. Woods, D. A. Shirley, and S. Avakian, *J. Am. Chem. Soc.*, **68**, 426 (1946).

(16) J. D. Roberts and D. Y. Curtin, *ibid.*, **68**, 1658 (1946).

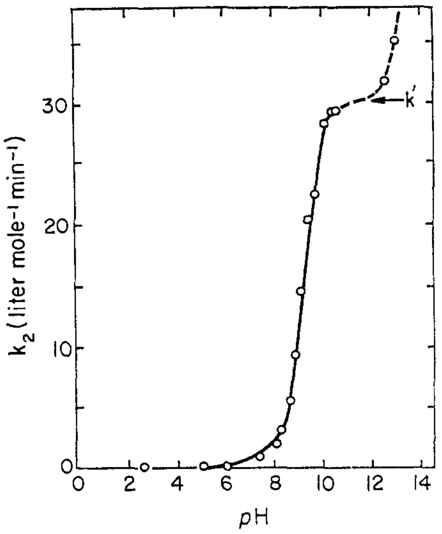

Figure 2. Relation between pH and the rate of the permanganate oxidation of benzylamine.

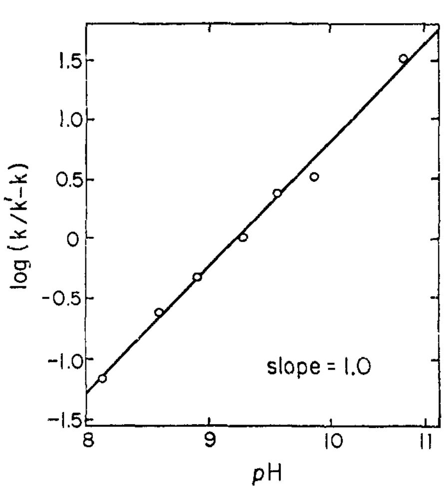

Figure 3. Plot of the function log $(k/(k' - k))$ against pH for the permanganate oxidation of benzylamine.

Results

In the pH region below 12, permanganate is reduced *via* a 3-equiv change to manganese dioxide. Benzylamine is initially oxidized by permanganate to benzalimine, which hydrolyzes to benzaldehyde or reacts with the parent benzylamine to form various polymers.[3,17] The stoichiometry for the first part of the reaction between permanganate and benzylamine can be represented as

$$3PhCH_2NH_2 + 2MnO_4^- \longrightarrow 3PhCH{=}NH + 2MnO_2 + 2H_2O + 2OH^-$$

Using stoichiometric quantities of permanganate and benzylamine the rate data were found to fit second-order integrated rate expressions over most of the pH range studied (Figure 1). The rate plots were linear in most cases up to at least 50% reaction before leveling off. In acidic solutions the rate plots are linear for approximately 20% reaction and then rise sharply in an autocatalytic manner. This latter phenomenon was partly subdued when a onefold excess of permanganate was added to oxidize the benzaldehyde that is formed. Oxidations of benzylamine at pH 10.43 with increasing concentrations of potassium sulfate (ionic strength varied from 0.4 to 1.2) showed no ionic strength effect on the rate of reaction.

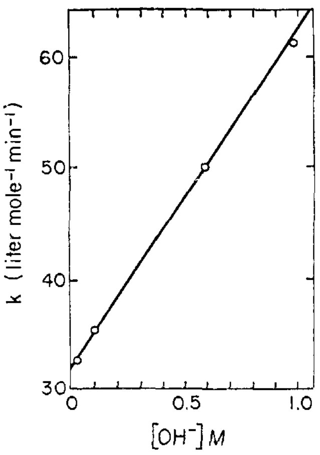

Figure 4. Relation between the hydroxyl ion concentration and the rate of the permanganate oxidation of benzylamine in alkaline solution.

The rate of benzylamine oxidation increases with increasing pH, but the dependence is not linear. A plot of the rate constant *vs.* pH produced a typical ionization curve (Figure 2).

It is very difficult to obtain satisfactory kinetics in the pH region 11–12.5 because the rate of the manganate disproportionation becomes comparable to the oxidation rate.

The curve in Figure 2 suggests that neutral benzylamine is the active reductant. If this is the case one can show that a plot of log $(k/(k' - k))$ *vs.* pH, where k' is the first rate maximum (Figure 2), should give a straight line of unit slope whose intercept is the pK_{BH^+} of the benzylammonium ion. Figure 3 shows that this relation is indeed obeyed, and the pK_{BH^+} of benzylamine is 9.28, very close to the literature value of 9.34.[18]

Although the rate–pH profile for the oxidation of benzylamine leveled off in the region pH 11 to 12 as all the ammonium ion was converted to free amine, a further increase in rate occurred in strongly basic media. The rates from pH 13 to 14 were found, in fact, to increase linearly with increasing hydroxyl ion concentration (see Figure 4). The extrapolated rate constant at $[OH^-] = 0$ was 32 l. mole^{-1} min^{-1} which corresponded approximately to the oxidation rate constant obtained at the maximum of the dissociation curve of benzylammonium ion.

In the highly basic region the intermediate, benzaldehyde, is rapidly degraded to benzoic acid by both permanganate and manganate, whereas oxidation of benzylamine by manganate is much slower. The correct ratio of substrate to permanganate on this basis is 3:4. The actual ratio used in the kinetic runs was 1:2, and a rate expression correcting for the presence of excess permanganate was derived.[4,6]

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(17) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **85**, 2843 (1963).

(18) F. Kieffer, *Compt. Rend.*, **238**, 1043 (1954).

$$k_2 = \frac{-4.60}{[\text{amine}]_0 t} \log \frac{V_t - \frac{3}{5}V_0}{V_t - \frac{2}{5}V_0}$$

Plots of the logarithmic function against time were linear.

Activation Parameters. A series of rate measurements was carried out at various temperatures at pH values where the amines were largely unprotonated so that minimal corrections were required for the effect of changing temperature on the ionization process. The activation parameters are shown in Table I.

Table I. Permanganate Oxidation of Benzylamine. Activation Parameters

$X\text{-}C_6H_4CH_2NH_2$	ΔH^*, kcal/mole	ΔS^*, eu
$p\text{-}CH_3$	11.7 (11.3)	−21.6
H	11.0	−22.5
$m\text{-}CF_3$	11.3 (11.7)	−21.9
$p\text{-}NO_2$	10.4	−24.8

Isotope Effects. Benzylamine-α-d_2, $C_6H_6CD_2NH_2$, was oxidized in the pH range 8 to 11 and the plot of k_2 *vs.* pH also gave a typical ionization curve. A unit slope was obtained from a log $(k/(k' - k))$ *vs.* pH plot, and the intercept gave a pK_{BH^+} of 9.41. The mean isotope effect in this region, k_H/k_D, was found to be 7.0.

Benzylamine-N,N-d_2, $C_6H_5CH_2ND_2$, was oxidized in D_2O at pH 10.4 (uncorrected glass electrode reading) where benzylamine is almost completely in the neutral form so that the isotope effect on the degree of ionization of the amine will be negligible. There was no detectable difference in rate between the reactions conducted in H_2O and D_2O.

Substituent Effects. To obtain information regarding the electronic requirements at the α carbon, 11 *meta-* and *para*-substituted benzylamines were oxidized at pH values where their degrees of ionization were small. The rate constants were then corrected for partial ionization using pK_{BH^+} values calculated from the work of Blackwell, *et al.*[19] A very poor Hammett correlation is obtained when log k is plotted against σ values. However, when log k is plotted against σ^+ values all the points fall on a straight line with the exception of *m*-trifluoromethylbenzylamine, *m*-nitrobenzylamine, and *p*-nitrobenzylamine (Figure 5). A least-squares treatment, excluding the three "anomalous" points, gives a slope of −0.28.

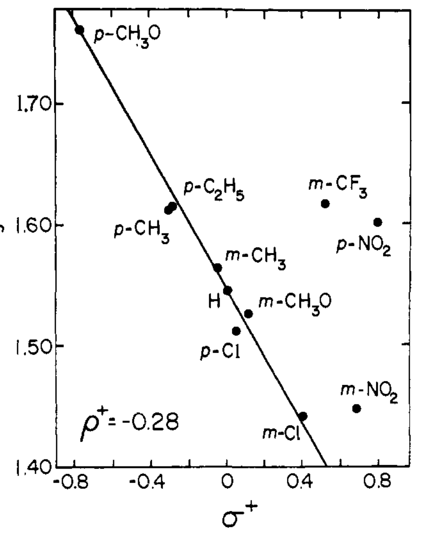
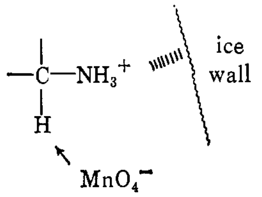


Figure 5. Effect of substituents on the rate of the permanganate oxidation of substituted benzylamines.

To determine if the exalted rate for *p*-nitrobenzylamine might be due to some condensation reaction between the amino and the nitro groups prior to the oxidation step, a solution of equimolar amounts of benzylamine and nitrobenzene at pH 10.1 was oxidized with permanganate. No difference was found in the rates for the solution containing nitrobenzene and that containing none.

A test was also carried out to determine whether the acetate ion might have any effect on the oxidation rates since the stock solutions of some of the amines were prepared from the amine acetate salts. No change in rate was again observed for benzylamine solutions containing no sodium acetate and for those containing equimolar amounts of sodium acetate at pH 10.10.

Frozen Systems. A number of cases have recently been reported of rate accelerations in frozen systems.[20,21] In Table II the oxidation rates are compared for systems that are identical except that in one case the reaction mixture is frozen at −10°. It is clear that freezing causes a considerable increase in the reaction rate. Since the active reductant in the liquid systems is amine, not ammonium ion, we thought, initially, that the increased rate found in the frozen systems at pH 8.25 might be due to a concerted process in which benzylammonium ion transfers a proton to the surrounding ice wall as the permanganate attacks the hydrogen atom of the α-methylene group. Further



examination revealed, however, that the rate in the frozen systems is also pH dependent and the increased rates cannot be accounted for in terms of a concerted oxidation of the ammonium ion.

Table II. Comparison of Rates of Benzylamine and *p*-Nitrobenzylamine in Liquid and in Frozen Systems.[a] k_2 in l. mole^{-1} min^{-1}

Benzylamine pH	k_2 (25°, liquid)	k_2 (−10°, ice)	k_2 (−10°, liquid)[b]
9.31	14.5	15.1	1.3
8.25	2.96	5.02	0.22
7.53	0.350	0.834	0.045

[a] The pH values refer to aqueous solution at 25°. [b] Calculated from activation energy.

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(19) L. F. Blackwell, A. Fischer, I. J. Miller, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 3588 (1964).

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

(21) R. E. Pincock and T. E. Kiovsky, *ibid.*, **87**, 2072 (1965).

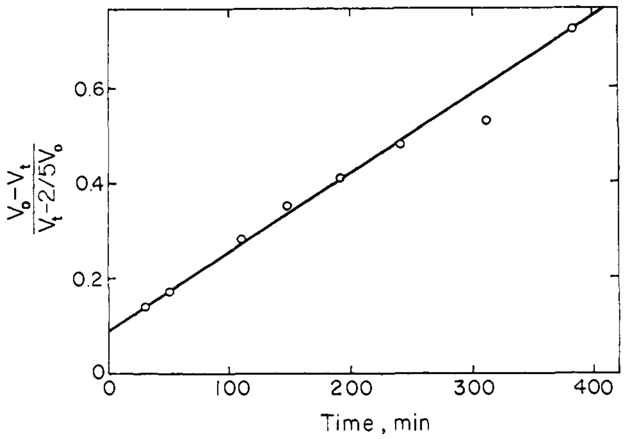

Figure 6. Second-order rate plot for the permanganate-benzylamine reaction at −10° in ice; pH 7.53 (at 22°).

Reasonably good kinetics were obtained for the reactions in frozen systems (Figure 6). However, in most of the rate plots, the line did not pass through the origin. Moreover, the departure from the origin increased as the pH of the solution increased. This may be due to the fact that during the preparation of the samples, which usually took about 3 min, the reaction was already occurring in the liquid state. This assumption is reasonable, since in the oxidation of benzylamine at 25° at pH 7.53, the percentage reaction at 3 min corresponded almost exactly to the percentage reaction at zero time for the frozen run. Since these studies in the frozen systems were rather exploratory in nature, all the possible errors inherent in the technique have not been entirely eliminated, although attempts to minimize them as much as possible were made.

If the concentration of free amine in the frozen systems is calculated using the ionization constant for solution at 25° ($pK_{BH^+} = 9.28$) a linear plot of log $[C_6H_5CH_2NH_2]$ *vs.* log k is obtained; the slope, however, is 1.37. Using an "apparent pK_{BH^+}" of 8.70 for benzylamine a linear plot of unit slope is obtained.

It is not obvious at present whether the accelerated rates obtained in frozen systems are due to a reaction in the solid state or to a concentration of the reactants in pockets of liquid in the ice lattice, although the latter explanation appears to be correct in other cases.[21] However, a kinetic run at pH 8.30 in which a large excess of sodium sulfate was added (0.6 *M*) showed no change in rate compared to the reaction without added salt at the same pH, and this is surprising if the reaction occurs in liquid pockets since one would expect some sort of alteration in the concentrations of the liquid reactants under these conditions.

Discussion

The kinetics are consistent with a mechanism which involves the reaction of permanganate ion and the neutral amine in the rate-determining step. The

$$C_6H_5CH_2NH_2 + H_2O \overset{K}{\rightleftharpoons} C_6H_5CH_2NH_3^+ + OH^-$$

$$C_6H_5CH_2NH_2 + MnO_4^- \xrightarrow{k} \text{products}$$

oxidation of the benzylammonium ion is extremely slow, the rate of benzylamine oxidation exceeding that of benzylammonium ion oxidation by a factor of between 10^3 and 10^4.

Although neutral amines are oxidized very much faster than neutral alcohols by permanganate, they are in general oxidized more slowly than are the anions of alcohols. The anions of amines presumably would be extremely reactive toward permanganate. The higher oxidation rate that is observed as the pH is raised from 12 to 14 indicates a second reaction exists. It seems most unlikely that the hydroxyl ion dependence is due to the ionization of the benzylamine molecule, however, since the amino protons are far too weakly acidic to be sufficiently ionized at pH 14. Aniline has a pK_a of about 27[22] and benzylamine should be an even weaker nitrogen acid. Hence if the reaction were even diffusion controlled, the concentration of the benzylamine anion, $C_6H_5CH_2NH^-$, would still not be nearly high enough to produce the observed rate. It is also doubtful whether a proton can be removed from the α carbon of benzylamine at pH 14. The half-life of the ionization of *p*-nitrobenzylamine is approximately 30 min at $H_- = 17.9$,[22] and one would expect the ionization of benzylamine at pH 14 to be much slower. Hence the rise in rate beyond pH 12 cannot be due to the partial formation of the benzylamine carbanion.

It seems likely that the reaction in strongly basic solution is a termolecular one involving permanganate ion, neutral amine, and hydroxyl ion. The base could remove a proton from the amino group as the oxidant attacks the methylene group, or *vice versa.* For example, proton loss from the methylene could be accompanied by hydride, hydrogen atom, or electron loss from the amino group. Further work is required to elucidate the reaction path in strongly basic solution.

The entropies of activation for the principal reaction at pH < 12 are at first glance unexpected. The very large negative ΔS^* values for the reaction of the neutral amine with permanganate ion are of the same order of magnitude as the ΔS^* values for anions with permanganate.[4,6,23,24] In general, when two anions come together to form the activated complex the resulting ΔS^* for the reaction is large and negative. However, in this respect, previous studies of the reaction of neutral molecules with permanganate have also revealed rather large negative entropies of activation. The ΔS^* for the reaction of MnO_4^- and H_2 is −17 eu[25] and ΔS^* for the reaction of neutral formic acid with permanganate is −19 eu.[24] For all these reactions involving a neutral substrate with permanganate, one can postulate an ionic transition state which has extensive charge separation resulting from the transfer of either electrons or hyride ions. In the case of benzylamine the activated complex may be represented as in eq 1. The observed isotope effects are in agreement with such a transition state but give no information as to whether the transferred group is a hydrogen atom or a hydride ion, *i.e.*, whether the transition state collapses to manganese(VI) and a radical or to manganese(V) and the protonated imine. There is no doubt that the amino group strongly activates the adjacent methylene and this supports the idea of hydride transfer.

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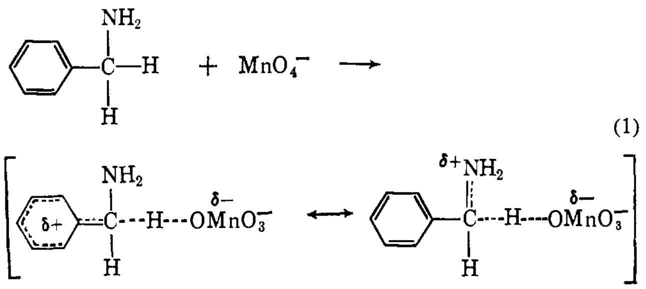
(22) D. Dolman and R. Stewart, to be published.

(23) R. Stewart and M. M. Mocek, *Can. J. Chem.*, **41**, 1160 (1963).

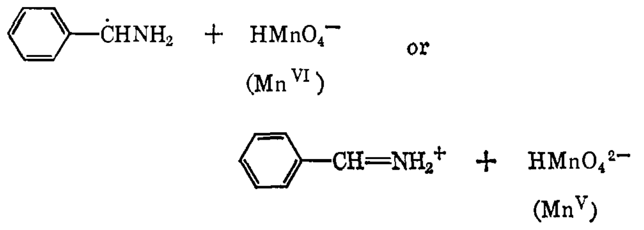
(24) S. M. Taylor and J. Halpern, *J. Am. Chem. Soc.*, **81**, 2933 (1959).

(25) A. H. Webster and J. Halpern, *Trans. Faraday Soc.*, **53**, 51 (1957).



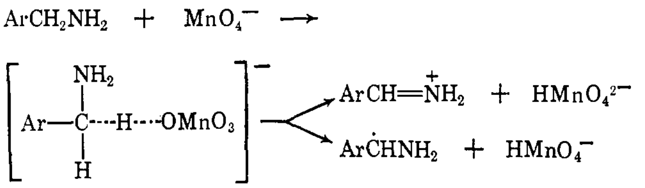
(1)

The fairly good $\rho\sigma^+$ correlation is also in agreement with hydride transfer since the positive charge in the protonated amine can be dispersed to the aromatic ring.[26]



The ρ^+ is quite small, however (−0.28), and furthermore three of the substituents (m-NO_2, p-NO_2, and m-CF_3) give much faster rates than their substituent constants would lead one to predict.

One can rationalize the activation due to p-NO_2 by saying that a hydrogen atom transfer also takes place in this case since the intermediate radical could disperse its odd electron to the substituent ($O_2NC_6H_4\dot{C}HNH_2 \longleftrightarrow \cdot O_2N{=}C_6H_4{=}CNNH_2$). The activation by m-NO_2 and m-CF_3 is more troublesome. Possibly the distinction between hydrogen atom and hydride ion transfer is not clear-cut. To be sure, one path leads to a radical intermediate and the other to a cation intermediate and this means that two distinct paths can be envisaged for the over-all reaction. However, the structure of the activated complex will be almost identical for the two paths and it seems preferable to consider a single activated complex whose decomposition to the two types of products is nicely balanced. The decomposition route would be influenced by many factors, including probability, vibrational effects in the activated complex, and the electronic effect of any substituents. The radical would be subject to immediate further oxidation (presumably to the imine conjugate acid) and the manganese species to disproportionation.



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[26] The odd electron may also be dispersed but whether a $\rho\sigma^+$ correlation would be expected is less certain, although precedents for such an effect do exist.[27]

[27] G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960); G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

Dicyanocarbene[1]

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Abstract: Dicyanocarbene, generated thermolytically from dicyanodiazomethane, inserts into the primary, secondary, and tertiary C–H bonds of n-butane and isobutane in the relative ratios of 1 : 4.6 : 12.0. Addition of the carbene to *cis*- and *trans*-2-butene proceeds nonstereospecifically, the formation of nonstereospecific adducts increasing with increasing dilution of the butenes with cyclohexane. At high dilution, an identical mixture containing 70% *trans*- and 30% *cis*-2,3-dimethyl-1,1-dicyanocyclopropane is obtained from either of the two isomeric olefins. Addition of dicyanocarbene to acetylenes yields 3,3-dicyanocyclopropenes. The nmr spectra of some of the products are discussed.

Dicyanocarbene is of interest as a highly electrophilic divalent species.[2] Its study became feasible with the recent synthesis of dicyanodiazomethane.[3] The present paper describes the reactions of dicyanocarbene with saturated hydrocarbons and with olefinic and acetylenic compounds.

Results

Dicyanodiazomethane (**1**) loses nitrogen readily, either on heating to about 70°, or on irradiation with ultraviolet light. In view of the facile thermal decomposition, this method of generating dicyanocarbene was used almost exclusively. In the single exception, namely in the decomposition of dicyanodiazomethane in benzene,[1] both methods gave the same product in identical yields. No solvent could be found that did not react with dicyanocarbene. Reactions were thus carried out using the substrates as

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[1] A preliminary communication describing the addition of dicyanocarbene to aromatic hydrocarbons appeared in *J. Am. Chem. Soc.*, **87**, 652 (1965).

[2] For an excellent review on carbenes, see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[3] E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).