

The Kinetics and Mechanism of the Oxidation of Benzyl Alcohol to Benzaldehyde by Bromine¹

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The kinetics of the oxidation of benzyl alcohol to benzaldehyde by bromine have been measured in several acetic acid-water solvents of varying proportions and with added buffer salts. The rate of oxidation is influenced by polar substituents such that the reaction constant for benzyl alcohol and nine monosubstituted derivatives has the value $\rho = -2.29$ at 25 °C with correlation coefficient $r = 0.9935$. Whereas the rate of oxidation of benzyl alcohol is linearly related to solvent composition, and is undetectable in anhydrous acetic acid, reaction constants in 25–95% (v/v) acetic acid-water mixtures are invariant. Activation enthalpies and entropies for 11 benzyl alcohols are linearly related with correlation coefficient $r = 0.9768$. Benzyl alcohol is oxidised by bromine at a rate 4.1 times faster than $\alpha\alpha$ -dideuteriobenzyl alcohol at 25 °C. The results are discussed in terms of a mechanism involving rate-determining removal of hydride ion from C(1)-H with the possibility of a synchronous removal of hydroxylic proton.

DENO and POTTER have suggested a basic similarity in terms of the reaction mechanism leading to the oxidation of alcohols² and ethers³ by bromine and by chromic acid. In contrast, the mechanism generally accepted for the oxidation of alcohols, aldehydes, and ethers by (partly) aqueous solutions of bromine differs from the chromic acid oxidations⁴ in that it involves as a main feature the oxidative removal of the hydrogen atom from C(1)-H as a hydride ion, rather than as a proton (see, e.g., refs. 5–9). The effective oxidising species in these reactions is molecular bromine rather than hypobromous acid¹⁰ and the reaction path does not involve organic hypobromites as intermediates.^{11,12}

Unlike aliphatic aldehydes, the oxidation of benzaldehyde probably involves two stages which together control the rate, the first being hydration of the aldehyde followed by oxidative removal of hydride ion from C(1)-H.¹³ The hydration step is not rate-controlling in the case of aliphatic aldehydes because they are rapidly and substantially hydrated.^{14,15} The oxidative removal of hydrogen from C(1)-H in alcohols and aliphatic aldehyde hydrates by bromine is probably the only rate-controlling stage. There is evidence that the loss of

hydroxylic proton to an external base is concerted with the hydride removal in the case of aliphatic aldehydes.¹⁶ Reactions at low acidities may involve the easily oxidised alkoxide ions derived from alcohol or aldehyde hydrate.¹⁰

The mechanism of oxidation by hydride removal proceeds from a logical deduction of indirect evidence. If it is assumed that the removal of hydrogen from C(1)-H is the slow and first stage of the reaction then an unequivocal demonstration of the direction of electron flow leading to the transition state can be obtained from the effect of polar substituents upon the reaction rate of a suitable alcohol.

This paper reports a detailed study of the kinetics of the oxidation of substituted benzyl alcohols by bromine and evaluates the reaction constant. The mechanistic conclusions are discussed.

RESULTS

In a solution of aqueous buffer (0.3M-NaOAc and HOAc) at pH 5, benzyl alcohol and bromine react eventually in the molar ratio 1 : 3, respectively. The product is *p*-bromobenzoic acid which was isolable in >90% yield. The reaction of benzyl alcohol (0.0486M) with bromine (0.00442M)

¹ Preliminary communication, P. Aukett and I. R. L. Barker, *Chem. and Ind.*, 1967, 193.

² N. C. Deno and N. H. Potter, *J. Amer. Chem. Soc.*, 1967, **89**, 3555.

³ N. C. Deno and N. H. Potter, *J. Amer. Chem. Soc.*, 1967, **89**, 3550.

⁴ 'Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965.

⁵ I. R. L. Barker, *Chem. and Ind.*, 1964, 1936.

⁶ C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Amer. Chem. Soc.*, 1961, **83**, 1945.

⁷ R. M. Barter and J. S. Littler, *J. Chem. Soc. (B)*, 1967, 205.

⁸ B. Perlmutter-Hayman and Y. Weissman, *J. Amer. Chem. Soc.*, 1969, **91**, 668.

⁹ P. T. McTigue and G. M. Sime, *J. Chem. Soc.*, 1963, 1303.

¹⁰ B. Perlmutter-Hayman and Y. Weissman, *J. Amer. Chem. Soc.*, 1962, **84**, 2323.

¹¹ L. Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 4645.

¹² L. Kaplan, *J. Amer. Chem. Soc.*, 1958, **80**, 2639.

¹³ I. R. L. Barker and R. H. Dahm, *J. Chem. Soc. (B)*, 1970, 650.

¹⁴ R. P. Bell, M. H. Rand, and K. M. A. Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 1093.

¹⁵ P. Greenzaid, Z. Rappoport, and D. Samuel, *Trans. Faraday Soc.*, 1967, **63**, 2131.

¹⁶ B. G. Cox and P. T. McTigue, *Austral. J. Chem.*, 1964, **17**, 1210.

in this solvent is of the first order in free bromine and had a rate constant of $10^3 k_2 = 7.23 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25 °C. The Volhard method applied to the analysis of bromide at completion of the conversion of benzyl alcohol into *p*-bromobenzoic acid confirmed quantitatively that bromine was consumed in both substitution and oxidation reactions.

Benzaldehyde reacted with bromine in the aqueous buffer and benzoic acid was isolated in good yield as the only organic product. Quantitative analysis of bromide ion showed that oxidation only had taken place. The reaction of benzaldehyde (0.0295M) with bromine (0.0274M) is of the first order in free bromine and has a rate constant of $10^3 k_2 = 2.12 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25 °C.

The experiments indicate a reaction in which benzyl alcohol is initially substituted by bromine to the *p*-bromoderivative and that this is oxidised consecutively to *p*-bromobenzaldehyde and *p*-bromobenzoic acid. *p*-Chlorobenzyl alcohol was also shown to be an unsuitable substrate for kinetic measurements in the aqueous buffer. In this case spectroscopic analysis of both compounds in the same run indicated that the consumption of bromine was substantially greater than the prevailing concentration of *p*-chlorobenzaldehyde. The reaction of *m*-nitrobenzyl alcohol with bromine in the aqueous buffer involved complex kinetics as the rate coefficients based on the loss of bromine increased markedly during the reaction. It was concluded that a study of the kinetics of the oxidation of benzyl alcohols to benzaldehydes was not feasible in this aqueous buffer and probably not in other fully aqueous solutions of similar low acidity.

In solvents of composition 1 : 1, 1 : 3, and 3 : 1 (v/v) acetic acid–water, bromine exclusively oxidised benzyl alcohol to benzaldehyde in high yield as shown by isolation of the product and Volhard determination of bromide ion. All kinetic experiments were subsequently carried out in acetic and aqueous acetic acid as solvents. The rate constants for the oxidation of benzyl and *p*-nitrobenzyl alcohols in 1 : 1 (v/v) acetic acid–water at 25 °C were $10^4 k_2 = 13$ and $0.23 \text{ l mol}^{-1} \text{ s}^{-1}$ respectively, whereas the rate constants for the similar oxidation of benzaldehyde and *p*-nitrobenzaldehyde were $10^4 k_2 = 1.43$ and $3.5 \text{ l mol}^{-1} \text{ s}^{-1}$ respectively. Although the rate constant for oxidation of *p*-nitrobenzaldehyde is greater than that of the corresponding alcohol, the kinetic importance of this may be reduced to an acceptable level by using a concentration of alcohol many times that of bromine.

Bromine is known to react with aqueous acetic acid.¹⁷ The consumption of bromine by the acetic acid–water mixtures and anhydrous acetic acid used as solvents was measured with similar concentrations of bromine, temperatures, and reaction times as in the kinetic runs. Only in anhydrous acetic acid containing added bases such as sodium acetate or pyridine was the loss of bromine to solvent large enough to prevent the reaction of bromine with benzyl alcohol from being studied. In anhydrous acetic acid, oxidation of benzyl alcohol (0.266M) by bromine (0.005M) at 35 °C could not be detected as the rate of loss of bromine was very slow (3.3% less bromine in 3 h) and paralleled that in the solvent alone.

When bromine reacts with a large excess ($\times 10$ or greater) of benzyl alcohol, the rate of consumption of bromine is of the first order in free bromine. The order with respect to concentration of benzyl alcohol was shown to be unity

(Table 1). For convenience of analysis and to limit oxidation of the benzaldehyde product, most runs were arranged to be of pseudo-first-order in bromine. Similar rate constants were obtained by spectroscopic measurements (at

TABLE 1

Kinetic order with respect to concentration of benzyl alcohol. Second-order rate constants/for the reaction of benzyl alcohol with bromine (ca. 0.005M) in 1 : 1 (v/v) acetic acid–water at 25 °C

$10^2 [\text{PhCH}_2\text{OH}]/\text{M}$	4.97	8.37	9.89	14.1	16.3	21.4
$10^3 k_2/\text{l mol}^{-1} \text{ s}^{-1}$	1.30	1.24	1.27	1.31	1.29	1.32

253 nm) of the rate of increase in concentration of the product, benzaldehyde. For example, compare the rate constants in Table 1 with the value $10^3 k_2 = 1.29 \text{ l mol}^{-1} \text{ s}^{-1}$ obtained in the above manner from the reaction of bromine (0.0649M) with benzyl alcohol (0.00197M) in 1 : 1 (v/v) acetic acid–water at 25 °C.

The rate constants for the oxidation of benzyl alcohol and

TABLE 2

Second-order rate constants at several temperatures, and entropies and enthalpies of activation for the oxidation of monosubstituted benzyl alcohols (0.1–0.3M) with bromine (ca. 0.005M) in 1 : 1 (v/v) acetic acid–water

Substnt.	$10^5 k_2/\text{l mol}^{-1} \text{ s}^{-1}$			$-\Delta S^\ddagger$	ΔH^\ddagger	r^a
	25 °C	35 °C	45 °C	$\text{cal mol}^{-1} \text{ K}^{-1}$	kcal mol^{-1}	
H	130	267	605	25.2	13.9	0.99837
<i>p</i> -F	42.4	102	240	21.2	15.7	0.99997
<i>p</i> -Cl	57.4	124	280	25.4	14.3	0.99936
<i>p</i> -Br	42.2	106	269	17.5	16.8	0.99976
<i>m</i> -F	24.0	59.4	146	20.1	16.4	0.99987
<i>m</i> -Cl	23.8	49.0	150	19.1	16.7	0.98920
<i>m</i> -Br	15.7	39.1	106	17.7	17.4	0.99901
<i>p</i> -CO ₂ Et	12.1	37.1	122	5.90	21.0	0.99921
<i>p</i> -CN	5.40	16.3	36.5	19.6	17.4	0.99729
<i>m</i> -NO ₂	3.13	8.38	38.9	1.77	23.1	0.98915
<i>p</i> -NO ₂	2.29	6.10	17.4	17.8	18.5	0.99924

^a The coefficient r refers to the correlation of data in the Arrhenius-type plot used to evaluate ΔH^\ddagger .

TABLE 3

Hammett reaction constants (ρ) and correlation coefficients (r) for the oxidation of benzyl alcohols with bromine; data from Table 2

$-\rho$, 25 °C	2.10 ^a	2.29 ^b
r	0.9738	0.9935
$-\rho$, 35 °C	1.94	2.12
r	0.9740	0.9918
$-\rho$, 45 °C	1.73	1.91
r	0.9660	0.9874

^a For 11 compounds. ^b Excluding *p*-F.

TABLE 4

Second-order rate constants and reaction constants (ρ) with correlation coefficients (r) for the oxidation of monosubstituted benzyl alcohols (0.06–0.3M) with bromine (0.005M) in several acetic acid–water solvents at 35 °C

H ₂ O/(% v/v)	75	50	25	5
$-\rho$	2.15	2.18	2.05	2.17
r	0.98578	0.99555	0.99358	0.97801
Substituent	$10^5 k_2/\text{l mol}^{-1} \text{ s}^{-1}$			
H	390	267	127	21.3
<i>p</i> -Cl	201	124	61.5	9.80
<i>m</i> -Cl	113	49.0	31.3	3.44
<i>p</i> -NO ₂	10.0	6.10	3.67	

¹⁷ J. Sevcik and J. Zyka, *Microchem. J.*, 1967, **12**, 472.

$\alpha\alpha$ -dideuteriobenzyl alcohol (both *ca.* 0.2M) with bromine (*ca.* 0.005M) in 1:1 (v/v) acetic acid-water at 25 °C were $10^4 k_2 = 12.6$ and $3.11 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively; the isotope ratio $k_H : k_D$ is 4.1.

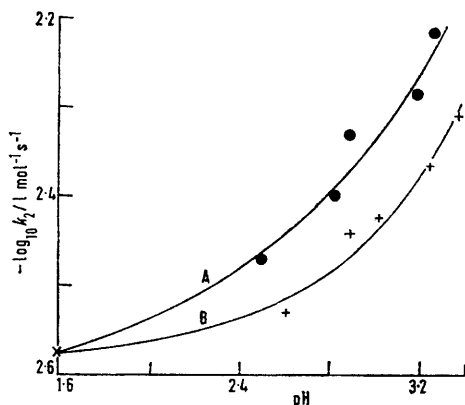
Other measurements are summarised in Tables 1–5 and the Figure.

TABLE 5

The influence of added salts on the second-order rate constants for the oxidation of benzyl alcohol (*ca.* 0.10M) with bromine (0.005M) in 1:1 (v/v) acetic acid-water at 35 °C

[CH ₃ CO ₂ Na]/M	0.0	0.1	0.2	0.2 ^a	0.3	0.4	0.5
pH	1.60	2.60	2.89	2.90	3.02	3.25	3.38
$10^3 k_2 / \text{l mol}^{-1} \text{ s}^{-1}$	2.67	2.96	3.63	3.62	3.78	4.35	4.93
[Na ₂ HPO ₄]/M	0.0	0.1	0.2	0.3	0.4	0.5	
pH	1.60	2.48	2.81	2.90	3.18	3.28	
$10^3 k_2 / \text{l mol}^{-1} \text{ s}^{-1}$	2.67	3.41	4.03	4.70	5.23	6.10	

^a In the presence of 0.3M-NaClO₄.



$\log k_2$ for the oxidation of benzyl alcohol at 35 °C in 1:1 (v/v) acetic acid-water in the presence of sodium dihydrogen phosphate (curve A) and sodium acetate (curve B); data from Table 5

DISCUSSION

Benzyl alcohol is oxidised with bromine at a rate 4.1 times faster than that of $\alpha\alpha$ -dideuteriobenzyl alcohol. The magnitude of $k_H : k_D$ may be compared with those reported for other oxidations, namely 3.9 for acetaldehyde (bromine; water; 25 °C),¹² 4.3 for ethanol (bromine; water; 25 °C),¹² 2.9 for propan-2-ol (bromine; aqueous buffer; 50 °C),⁶ 3.8 for formic acid (iodine; water; 21 °C),¹⁸ 2.2 for formic acid (iodine; dimethyl sulphoxide; 21 °C),¹⁸ and 2.5 for benzaldehyde (bromine; 1:1 AcOH-H₂O; 70 °C).¹³ The mechanistic conclusion is that the C(1)-H bond is broken during a rate-controlling step.¹⁹

Evidence presented by other authors mentioned earlier indicates that bromine and alcohol are not involved in a kinetically important rate of equilibrium stage before the removal of hydrogen from C(1)-H. In acidic media the hydroxylic proton may alternatively be removed after the breaking of C(1)-H or synchronously with it. A study of the effect upon rate constant of acidity and

buffer ions in a fully aqueous solvent was not possible in the case of the reaction of bromine with benzyl alcohol owing to the preference for substitution at low acidities.

The measurements with benzyl alcohol summarised in Table 5 and the Figure show that at a particular acidity the rate of oxidation depends upon the nature of the added buffer salt; the addition of the inert salt sodium perchlorate had no detectable effect. The presence of sodium borate also enhanced the rate of oxidation but it was insufficiently soluble to allow an extensive study to be performed. The results may be regarded as limited evidence for general base catalysis; however, the catalytic effect of each species cannot be evaluated as the dissociation constants of the salts in the solvent are not known. Further, the concentration of hydroxide ions cannot be accurately evaluated as the solution is non-ideal.

The rate constants for the oxidation of four benzyl alcohols (Table 4) vary linearly with solvent composition in acetic acid-water mixtures. The extrapolations of these lines to 100% acetic acid intersect at a rate constant of *ca.* 0. Experimentally, reaction of benzyl alcohol with bromine in anhydrous acetic acid could not be detected. Although it may be expected that the rate of oxidation with bromine should be dependent upon the dielectric constant of the solvent, the expectation is not borne out quantitatively. The dielectric constant for acetic acid-water mixtures¹⁷ varies in a non-linear manner from *ca.* 10 for acetic acid to 80 for water, and in the range *ca.* 10–65% acetic acid is greater than 100. An alternative explanation for the observed linear relationship in the oxidation is that water may be serving as a base to remove the hydroxylic proton in the rate-determining stage. Consequently, the rate of reaction has first-order dependence upon the concentration of water. A similar first-order dependence may be inferred from the rates of oxidation with bromine of butane-2,3-diol and acetoin, although the authors interpret this in terms of a dielectric effect.²⁰

No systematic study of the effect of substituents upon the rates of oxidation of benzyl alcohol with bromine has previously been reported.¹ Limited studies with aliphatic alcohols include the observation of Swain and his co-workers⁶ that propan-2-ol is oxidised *ca.* 1000 times more rapidly than 1-fluoropropan-2-ol. A reaction constant of $\rho^* = -2.6$ has been reported for substituted propan-2-ols.²¹ However, we observe that this value was derived from a Taft plot in which linearity was obtained at the expense of neglecting an experimental result and the inclusion of another taken from the paper by Swain and his co-workers.⁶ A Taft plot of data obtained in this study shows marked curvature.

We find that electron-withdrawing groups decrease the rates of oxidation of *meta*- and *para*-substituted benzyl alcohols and the results for ten compounds give

¹⁸ F. W. Hillier and J. H. Kreuger, *Inorg. Chem.*, 1967, **6**, 528.

¹⁹ F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

²⁰ N. Venkatasubramanian and A. Sabesan, *J. Indian Chem. Soc.*, 1966, **4**, 327.

²¹ N. Venkatasubramanian and V. Thiagarajan, *Tetrahedron Letters*, 1968, **14**, 1711.

good correlation in the Hammett plot with a reaction constant of $\rho = -2.29$ at 25 °C. The rate constant for *p*-fluorobenzyl alcohol deviates from the best line for the other ten compounds and requires a substituent constant of $\sigma = ca. 0.230$ to correlate.²² The activation parameters ΔH^\ddagger and ΔS^\ddagger (Table 4) display a linear relationship and give a line of best fit with correlation coefficient $r = 0.9768$. The correlation was tested and considered genuine²³ by applying Exner's criterion.²⁴ The slope of the correlation line for ΔH^\ddagger and ΔS^\ddagger is 371 K but current views do not attach important physical meaning to the isokinetic temperature.^{23,25}

Whereas the magnitude of the reaction constant predictably diminishes with increasing temperature (Table 3) it does not appear to vary with dielectric constant (Table 4) in the manner expected,²⁶ and found experimentally in other reactions.²⁷ In view of the polar nature of the oxidation with bromine the result is puzzling and no satisfactory explanation arises at present.

The results reported in this paper give direct evidence of a hydride-transfer mechanism in the oxidation of benzyl alcohol. Other measurements presented as in favour of a base-catalysed reaction are insufficiently substantial to confirm this feature and the interpretation is possibly inconsistent with the magnitude of the reaction constant. As the polar requirements upon the carbinol carbon of hydride release from C(1)-H and proton release from O-H are opposite, a fully concerted process might be expected to have a reaction constant nearer zero.

It is of interest to compare the reaction constant obtained with the value of $\rho = -2.5$ reported for the dehydrogenation of substituted 1,2-dihydronaphthalenes by tetrachloro-1,2-benzoquinone.²⁸ The suggested mechanism is multistage and involves initial formation of a charge-transfer complex, followed by a slow hydride transfer. The sign and magnitude of the reaction constant reflect the kinetic importance of the hydride-transfer stage. We observe that although the correlation of rate constants in the Hammett plot in this study²⁸ is acceptable, there is no correlation for ΔH^\ddagger versus ΔS^\ddagger where the correlation coefficient is $r = 0.7087$ for the 14 compounds. An acceptable correlation is usually a necessary condition for the validity of the Hammett equation.

Another comparison is in the reduction of ketones to alcohols by borohydride which probably involves rate-

controlling addition of hydride ion. It is reported that the reaction constants for the rate of reduction of 2- and 4-substituted fluorenones by sodium borohydride are $\rho = +2.95$ and $+2.56$, respectively.^{29,30}

EXPERIMENTAL

Materials.—Halogeno-, *m*-nitro-, and *p*-cyano-substituted benzyl alcohols were prepared by reduction of the corresponding benzaldehydes with sodium borohydride.³¹ *p*-Ethoxycarbonylbenzyl alcohol was obtained by esterification of *p*-carboxybenzyl alcohol prepared by the reduction of *p*-carboxybenzaldehyde with sodium borohydride. Benzyl and *p*-nitrobenzyl alcohol were commercial. The alcohols were purified by repeated crystallisation or by distillation under reduced pressure under nitrogen. All m.p.s and b.p.s were in good agreement with literature values.³²⁻³⁵ Purity was confirmed by their i.r. spectra, particularly the absence of the strong carbonyl stretching band at *ca.* 1700 cm⁻¹.

$\alpha\alpha$ -Dideuteriobenzyl alcohol was prepared by reducing ethyl benzoate with lithium aluminium deuteride.³³ The isotopic purity of the compound was ascertained from its i.r. and n.m.r. spectra.

Acetic acid of analytical reagent grade was found to contain impurities which rapidly consume bromine at 45 °C. These were removed by the method of Orton and Bradfield.³⁴ Anhydrous acetic acid was obtained by the method of Birdwhistell and Griswold.³⁵ Analytical reagent grade bromine was used without further purification.

Kinetic Procedures and Calculation of Results.—Most runs were followed by quantitative analysis of bromine in the reaction mixture. It was eventually established that spectrophotometric analysis gave rate constants identical to those of the titrimetric method using iodine and sodium arsenite and the former method was selected. In acetic acid-water solvents quantitative analysis of bromine was carried out at a wavelength of 450 nm rather than the customary 398 nm, the wavelength of maximum absorption. The reason for this is based on a consideration of the following factors: (a) the oxidant is free bromine and not tribromide ion, (b) the equilibrium constant for tribromide ion formation is several times larger in aqueous acetic acid³⁶ than in water,³⁷ (c) the extinction coefficients of bromine and tribromide ion in 1 : 1 (v/v) acetic acid-water at 25 °C are as follows: ²³ at 398 nm, $\epsilon(\text{Br}_3^-)$ is 569 and $\epsilon(\text{Br}_2)$ is 187; at 450 nm, $\epsilon(\text{Br}_3^-)$ is 106 and $\epsilon(\text{Br}_2)$ is 110; at 470 nm, $\epsilon(\text{Br}_3^-)$ is 49, $\epsilon(\text{Br}_2)$ is 79. At 450 nm, the two species contribute with almost equal weight to the total optical density. Consequently, the rate constants obtained by following the loss of bromine spectrophotometrically at this wavelength parallel those obtained titrimetrically.

²² H. van Bekkum, T. D. Werkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

²³ For details see P. Aukett, Ph.D. Thesis, Brighton Polytechnic, 1970.

²⁴ O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29** (5), 1094.

²⁵ J. E. Leffler, *J. Org. Chem.*, 1966, **31**, 533.

²⁶ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

²⁷ E. Tommila, *Ann. Acad. Sci. Fennicae*, 1967, Ser. A II, **139**, 69.

²⁸ L. M. Jackman and D. T. Thompson, *J. Chem. Soc.*, 1961, **4794**.

²⁹ J. A. Parry and K. D. Warren, *J. Chem. Soc.*, 1965, 4049.

³⁰ K. D. Warren and J. R. Yandle, *J. Chem. Soc.*, 1965, 5518.

³¹ A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1962.

³² 'Dictionary of Organic Compounds,' eds. I. Heilbron and H. M. Bunbury, Eyre and Spottiswoode, London, 1953; K. Fukui, H. Kitano, T. Osaka, Y. Inamoto, and H. Shirai, *Chem. Abs.*, 1960, **54**, 5518; J. N. Ashby, H. J. Barber, A. J. Ewins, G. Newberry, and A. D. H. Self, *J. Chem. Soc.*, 1942, 103; F. H. Case, *J. Amer. Chem. Soc.*, 1925, **47**, 1145.

³³ J. F. Bunnett, G. T. Davies, and H. Tamida, *J. Amer. Chem. Soc.*, 1962, **84**, 1606.

³⁴ K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 1924, 960.

³⁵ R. K. Birdwhistell and E. Griswold, *J. Amer. Chem. Soc.*, 1955, **77**, 873.

³⁶ E. Berliner and M. C. Becket, *J. Amer. Chem. Soc.*, 1957, **79**, 1425.

³⁷ T. Mussini and G. Faita, *Ricerca sci.*, 1966, **36**, 175.

Rate constants were calculated either from the appropriate integrated rate equations or from initial slopes drawn to expanded curves of time against concentration. All kinetic runs were carried out at least in duplicate with reproducibility within 5%. Where a linear relationship was considered a possibility between rate constants or a function of the rate constants and some other property of the reaction system, the line of best fit was obtained by the method of

least squares. The correlation of the data is expressed by the correlation coefficient which was calculated for each regression line.

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