[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XIV. The Effect of *p*H on the Rate of Hydrolysis of Chloroform[1]

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Horiuti, Tanabe and Tanaka have studied the effect of *p*H on the rate of hydrolysis of chloroform and reported a rather unusual *p*H-rate profile involving a rate maximum near *p*H 4.0. Since their reaction solutions were unbuffered the reaction was followed to only a *very* small fraction of completion. To learn whether this may have introduced an artifact into their results a reinvestigation has been carried out using buffer solutions. No evidence for the reported rate maximum was found and in fact, if corrections are made for S_N2 attack by the buffer anion, it is found that none of the log *k* values deviated from the mean by so much as 0.06 over the *p*H range 1.5 to 5.5. It is therefore suggested that in basic solution chloroform hydrolyzes *via* the intermediate dichloromethylene, and in acidic solution there is a first-order solvolysis that is probably largely S_N2 in character. It is pointed out that the rate of exchange of radioactive chloride ions with chloroform observed by Horiuti, Tanabe and Tanaka in acidic solution is reasonably near the rate that would be expected for the S_N2 attack of chloride ion on chloroform, and the rate in basic solution is reasonably near that which would be expected from the combination of dichloromethylene molecules with chloride ions.

Introduction

In earlier papers of this series evidence was presented that the basic hydrolysis of chloroform in aqueous solution proceeds by the mechanism

$$CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$$
$$CCl_3^- \longrightarrow CCl_2 + Cl^- \quad \text{(I)}$$

where the preliminary equilibrium is established rapidly compared to the rate of formation of dichloromethylene, a reactive intermediate that is transformed quickly into the final products, a mixture of carbon monoxide and formate ion.[2,3]

Upon examining the rate of chloroform hydrolysis over the complete range of *p*H's from fairly strongly acidic to fairly strongly basic solutions, Horiuti, Tanabe and Tanaka (referred to hereafter as HTT) reported a rather unusual relationship between *p*H and rate.[4] The idealized version of their plot of *p*H *vs.* log *k* is shown by the broken line in Fig. 1. At *p*H's above about 5.5, a straight line of slope +1 is obtained in agreement with our observation that the hydrolysis rate in basic solution is proportional to the hydroxide ion concentration. While we have not previously commented on the mechanism of hydrolysis in neutral and acidic solution, we would have expected that there would exist a solvolysis reaction whose rate was independent of *p*H and that at some sufficiently low *p*H where hydrolysis by mechanism I has become slow enough, this solvolysis reaction would become the principal reaction path. Since acid catalysis in the solvolysis of organic chlorides seems improbable in aqueous solution,[5] we would have expected Fig. 1 to have consisted of a line of slope zero starting at the lowest *p*H's used and continuing with increasing *p*H until intersection with the line of slope +1. Thus the features of Fig. 1 that seem anomalous to us are the increase in rate that reaches a maximum (with a rate about ten times that at lower *p*H's) at about *p*H 4.0 and the fact that the rate minimum near *p*H 5.5 corresponds to a rate somewhat slower than that at *p*H 0–3.

HTT have very ingeniously explained the entire plot of *p*H *vs.* rate in terms of a single hydrolysis mechanism (II) operating for the whole *p*H range.[4]

$$CHCl_3 + B \rightleftharpoons HB + CCl_3^-$$
$$CCl_3^- + HB' \rightleftharpoons Cl_2\overset{x}{\underset{x}{C}}ClH + B'$$
$$HA + Cl_2\overset{x}{\underset{x}{C}}ClH + B'' \longrightarrow$$
$$A + HCl + CCl_2 + B''H \quad \text{(II)}$$

where HA and HB are acids and A and B are bases, and dichloromethylene is a reactive intermediate that is quickly transformed to the final products. In the unbuffered aqueous solutions used the only bases present are hydroxide ion and water, and the only acids are hydronium ion and water. While there is not space here to describe the systematic and logical argument of HTT in detail, the *p*H profile was explained in terms of mechanism II briefly as follows: At low *p*H's the second step of the reaction is rate-controlling and for the line of zero slope the HB′ of step 2 is hydronium ion. As the *p*H increases, however, hydronium ion functions to a decreasing extent as HB′ in step 2 and by *p*H 3.0 the principal HB′ has become water. The increase in rate at *p*H 3.0 is due to this incursion of water as HB′. By *p*H 4.0 the third step of the reaction, in which HA has been hydronium ion and B″ water, has become so slow that it now becomes rate-controlling and the reaction rate decreases with increasing *p*H. At the point of minimum rate at about *p*H 5.0, HA becomes water and B″ is hydroxide ion. The points in this *p*H range had been difficult to determine. Since the reaction solutions were not buffered, the reaction of as much as 0.03% of the chloroform present would be sufficient to change the *p*H of the reaction solution from 6.0 to 3.0. Therefore the reactions at these *p*H's could only be carried a *very* small percentage of the way to completion. Accordingly, the reaction of a small amount of some reactive impurity (such as phosgene) in the chloroform could account for at least some of the observed data obtained at these *p*H's. In this regard, it should be mentioned that while an excellent job was done of removing oxygen from the sealed tubes in the reaction and freshly distilled chloroform was used, the chloroform had been distilled in air[6] and some phosgene formation seems possible.

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(1) For part XIII see J. Hine and F. P. Prosser, THIS JOURNAL, **80**, 4282 (1958).

(2) J. Hine, *ibid.*, **72**, 2438 (1950).

(3) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

(4) J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis, Hokkaido Univ.*, **3**, 119, 147 (1955); *C. A.*, **50**, 1428c,f (1956).

(5) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 165.

(6) Private communication from K. Tanabe.

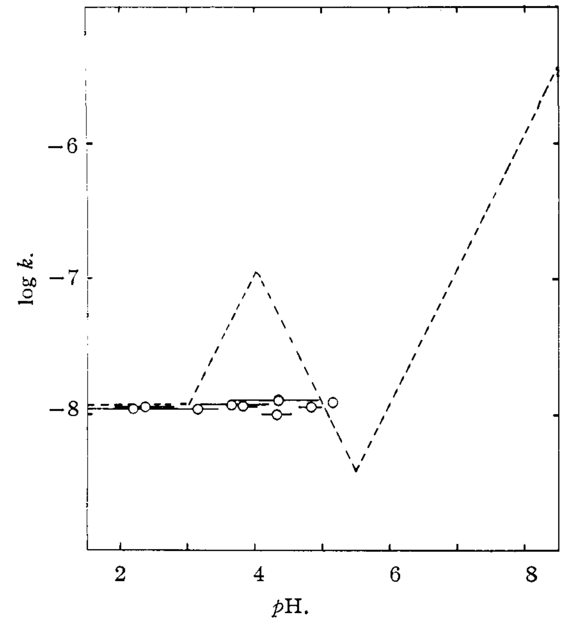

Fig. 1.—Relation between *p*H and the rate of hydrolysis of chloroform. Horiuti, Tanabe and Tanaka's *p*H profile shown by broken line, our results by the circles.

We therefore decided to reinvestigate this *p*H region by use of buffer solutions in order that the reactions could be carried to a much higher percentage of completion without excessive changes in *p*H. Although HTT had carried out the reaction under heterogeneous conditions at 100° with shaking, they found the reaction velocities to be independent of shaking rates and made the entirely plausible assumption that the reaction was taking place in the aqueous phase and that rates of diffusion of chloroform in and out of the aqueous phase were fast compared to the hydrolysis velocity. We therefore avoided the necessity of shaking by carrying out the reactions in homogeneous solution in sealed tubes at 100°, using acetic acid–acetate and formic acid–formate buffers. Since our buffered solutions at a given *p*H will contain all of the acids and bases (water, hydronium ion and hydroxide ion) that HTT's solutions did, all of the individual steps of reaction by their mechanism should proceed as fast or faster than in the absence of a buffer. Therefore if we compare the hydrolysis rate in buffered solutions at *p*H's around 3 to 6 with the rate in more acidic unbuffered solutions, it is possible that we shall find increases in rate where none would exist in the absence of a buffer but we should not be caused to overlook any rate maxima that would exist in the absence of a buffer.

We find no evidence for a rate maximum in the *p*H range investigated. To explain the difference between our results and those of HTT as a salt effect would require the assumption that the activated complex had an activity coefficient larger than ten. This seems to us to be unreasonable for a 0.2 *M* solution.

Results and Discussion

The Effect of *p*H on the Hydrolysis Rate.—In order to obtain data at a number of different *p*H's in the range 1.5 to 5.5, some kinetic runs were made using acetate buffers, some with formate buffers, and some with small concentrations of added strong acid. All runs were conducted at 100° and most at an ionic strength of 0.2. By extrapolation of the data of Harned and co-workers, the *pK* of acetic acid under these conditions is estimated as 4.975 and that of formic acid, 4.015,[7] with the effect of small changes in temperature and ionic strength being insignificant for our purposes. To determine first-order rate constants, for each run log ($[CHCl_3]_0/[CHCl_3]_t$) was plotted against time, as shown for two typical runs in Fig. 2. In each case the points fell reasonably near a straight line from whose slope the rate constant was calculated. While the rate constants may well be in error by as much as 10% they should be satisfactory for revealing a 10-fold increase in reactivity at a given *p*H. The results obtained are summarized in Table I. No significant effect of *p*H on rate appears. From the plots in Fig. 3 of *k vs.* the average concentration of buffer anion present during the run, a regular increase in rate with increasing buffer ion concentration is seen. While this should cause our calculated first-order rate constants to fall during each run as the buffer anion concentration falls, calculations show that this effect would be unnoticed since it would never amount to more than a 5% fall in any of our runs. We believe that this effect is due to the S_N2 attack[8] of the buffer anion on chloroform. From the slopes of the two lines in Fig. 3 the rate constant for the reaction of the acetate ion may be calculated to be 2.44×10^{-7} and that for formate ion 1.73×10^{-7} l. mole^{-1} sec.$^{-1}$. The first-order rate constants (k_1) obtained in the presence of an acetate buffer, for example, are therefore composite constants, having the form

$$k_1 = k_1^{\text{corr}} + k_{\text{OAc}^-}[\text{OAc}^-]_{\text{av}}$$

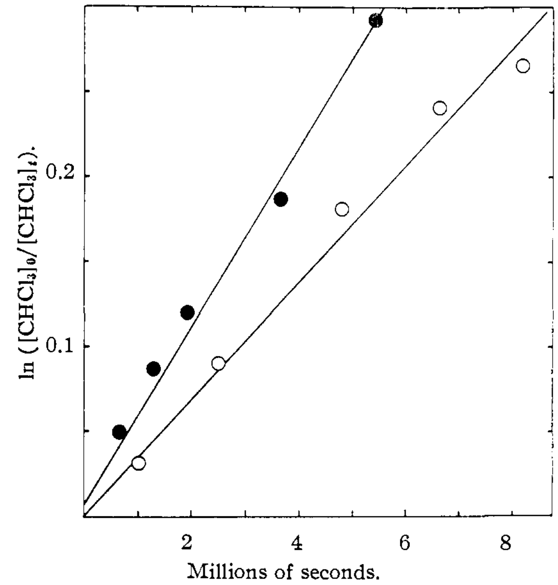

Fig. 2.—First-order rate equation plots. For solid circles, $[OAc^-]_0 = 0.1031$ *M*; for open circles, $[HCO_2^-]_0 = 0.048$ *M*.

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[7] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933); H. S. Harned and N. D. Embree, *ibid.*, **56**, 1042 (1934).

[8] For a discussion of the S_N2, S_N1 and intermediate reaction mechanisms, see ref. 5, chap. 5.

TABLE I

RATES OF HYDROLYSIS OF CHLOROFORM AT 100°[a]

$[\text{Acid}]_{\text{init}}$	$[\text{Base}]_{\text{init}}$	$[\text{Base}]_{\text{final}}$	$p\text{H}_{\text{init}}$	$p\text{H}_{\text{final}}$	10^8k_1	$10^8k_1^{\text{corr}}$
0.0709 HOAc	0.1321 OAc^-	0.0960	5.24	5.05	5.94	3.16
.0980 HOAc	.1031 OAc^-	.0737	5.00	4.70	5.24[b]	3.09
.0490 HOAc	.0516 OAc^-	.0033	5.00	3.69	4.10	3.43
.0423 HCO_2H	.1581 HCO_2^-	.1033	4.59	4.05	4.93[c]	2.67
.0995 HCO_2H	.1027 HCO_2^-	.0554	4.03	3.60	4.46[d]	3.09
.0345 HCO_2H	.0516 HCO_2^-	.0104	4.19	3.15	3.71	3.17
.1520 HCO_2H	.0480 HCO_2^-	.0109	3.51	2.78	3.45	2.94
.0010 HCl	None	None	3.00	1.70	3.10	3.10
.0011 HCl	None	None	2.94	1.42	2.85	2.85
					Av.	3.06 ± 0.16

[a] $[CHCl_3]_{\text{init}}$ was 0.0450 in the first run and 0.0499 in all others; rate constants are in sec.$^{-1}$. $f = 0.114$. [c] $f = -0.28$. [d] $f = 0.03$.

where k_1^{corr} is the rate constant for the first-order solvolysis of chloroform and k_{OAc^-} is that for second-order attack by acetate ions. We have therefore obtained k_1^{corr} values by subtraction of $k_{\text{OAc}^-}[\text{OAc}^-]_{\text{av}}$ (or $k_{\text{HCO}_2^-}[\text{HCO}_2^-]_{\text{av}}$) and these are listed in the last column of Table I. From a plot of runs 5–10 of Table 3 of the second article of HTT[4] the zero-order[9] rate constant for the hydrolysis of chloroform in acidic solution under their conditions may be estimated as 8.0×10^{-9} mole l.$^{-1}$ sec.$^{-1}$. We therefore have converted our rate constants to their scale by multiplication by 0.26, a figure which might be taken as the molar solubility of chloroform in water at 100° (it is about 0.07 at 20°) except for two complicating factors. First, our rate constants are probably somewhat too low because a sensibly constant but considerable fraction of the chloroform in our reaction tubes was probably in the vapor phase. Second, while both our reactions and those of HTT were maintained at "100°" by boiling water-baths, our laboratory is located about 1000 ft. higher than theirs. These factors considered, the agreement between the two sets of results seems satisfactory. Our converted rate constants are then compared with their pH profile in Fig. 1 where the ordinate of any point is log k and its abscissa is the mean pH during the run. The horizontal lines attached to the points indicate the entire pH range covered during the reaction. On the basis of these results we propose that at pH's below those at which the base-catalyzed dihalomethylene hydrolysis mechanism[2] is operative, the hydrolysis of chloroform occurs by a first-order pH-independent path.

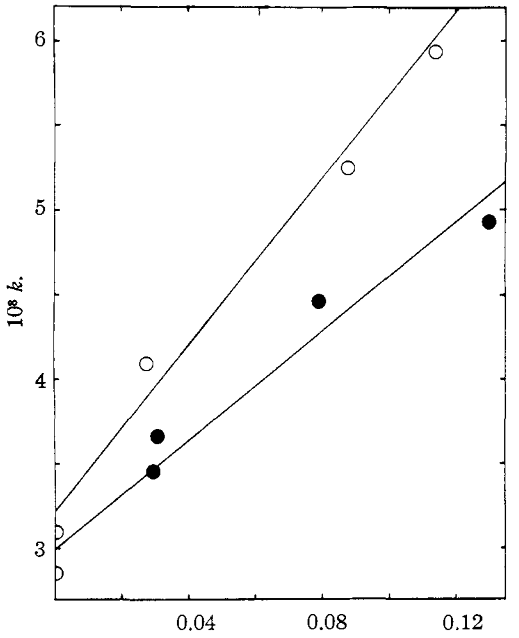

Fig. 3.—Plot of first-order rate constants for chloroform hydrolysis *vs.* concentration of buffer anion: open circles, acetate buffer; solid circles, formate buffer; half-circles, no buffer.

Mechanism of Hydrolysis and Chloride Exchange.—From our data on the effect of acetate and formate ions on the reaction rate we favor the view that the first-order hydrolysis of chloroform is largely SN2 in character.[8] The solvolysis of tertiary and other halides that react by the SN1 mechanism is not usually accelerated by the addition even of strong nucleophilic reagents. According to Hughes, Ingold and co-workers this shows that the solvent is not acting as a nucleophilic reagent in the solvolysis.[10] We feel that the distinct acceleration produced by these rather weak nucleophilic reagents shows that chloroform is sufficiently susceptible to such attack that the reaction with water should be largely SN2.

Our reaction mechanism differs from that of HTT not only in regard to the hydrolysis path but also in the explanation of the exchange of radioactive chloride ions. They have found this exchange to proceed at a constant rate at pH's up to about 6.0, above which log k increases linearly with the increasing pH, and have proposed that the pH-independent path involves an acid-catalyzed replacement of a chlorine atom in the trichloromethyl anion by external chloride ion

$$\text{Cl*}^- + \text{CCl}_3^- + \text{HA} \longrightarrow \text{Cl}^- + \text{Cl*CCl}_2^- + \text{HA}$$

where HA is H_3O^+, while at pH's above 6.0, HA becomes H_2O and the rate increases with the basicity. We believe, rather, that in acidic solution exchange occurs by the SN2 attack of chloride ion on chloroform and in basic solution it involves the capture

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(9) The kinetic order is zero because the chloroform concentration is maintained constant at the saturation point by the heterogeneous character of the reaction.

(10) *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, sec. 24c.

of intermediate dichloromethylene molecules by chloride ions.

$$CCl_2 + Cl^{*-} \xrightarrow{k_{Cl}} Cl^*CCl_2^- \longrightarrow CHCl_2Cl^*$$

$$CCl_2 + H_2O \xrightarrow{k_W} H_2\overset{\oplus}{O}\text{-}\overset{\ominus}{C}Cl_2 \longrightarrow CO \text{ and } HCO_2^-$$

While both sets of explanations fit all of the presently published data on the kinetics of the reaction, their relative merits may be assessed in several other ways. For example, we propose that the alkaline chloride exchange occurs by the same mechanism to which we have already attributed the "mass-law effect" by which chloride ions slow the rate of the basic hydrolysis of chloroform.[3] We are therefore able to use the values of k_{Cl}/k_W that we determined previously for 35°,[3] since such values do not change greatly with temperature,[11] to estimate the rate of chlorine exchange in basic solution provided that the solution is not so basic that an apprecible fraction of the dichloromethylene molecules are captured by hydroxide ion (we have no direct measurements of k_{OH^-}/k_W). According to our theory, under such conditions the rate of chlorine exchange should follow the relation

$$\frac{d[Cl^{*-}]}{dt} = \frac{k(k_{Cl}/k_W)[CHCl_3][OH^-][Cl^{*-}]}{[H_2O]} \quad (1)$$

where k is the second-order rate constant for the basic hydrolysis of chloroform

$$d[CHCl_3]/dt = k[CHCl_3][OH^-] \quad (2)$$

Dividing eq. 1 by eq. 2 and rearranging

$$\frac{d[Cl^{*-}]}{dt} = \frac{d[CHCl_3]}{dt}\left(\frac{(k_{Cl}/k_W)[Cl^{*-}]}{[H_2O]}\right)$$

Substituting the values 55 for $[H_2O]$, the average value (59) determined previously for (k_{Cl}/k_W) in dilute aqueous solution, and 0.01 for $[Cl^{*-}]$ we obtain

$$\log(d[Cl^{*-}]/dt) + 1.97 = \log(d[CHCl_3]/dt)$$

While the value 2.4 instead of 1.97 would be required for an optimum fit to the plots of hydrolysis rate and radio-chloride exchange rate in 0.01 *M* chloride, both in alkaline solution shown in Fig. 3 of the second paper of HTT, the agreement is believed to be reasonable in view of the approximations involved and the possible experimental error. This aspect of the comparison of the requirement of our mechanism with the experimental data is being studied further by M. Katayama. From the data of Table 3 of the first article of HTT on experiments carried out in acidic solution, the pseudo first-order rate constant for the reaction of chloride ion with chloroform is 8.5×10^{-9} sec.$^{-1}$. By comparison with HTT's rate constant (8×10^{-9} mole/l. sec.) we may calculate that the SN2 attack by chloride ion occurs about 58 times as fast as that by water molecules per mole of nucleophilic reagent present. Since we have found acetate ions to react about 430 times as fast as water molecules, the reactivity of chloride ions is slower than might be expected from the fact that Swain and Scott[12] list a nucleophilicity constant of 3.04 for chloride ion compared to 2.72 for acetate. The deviation, however, is no greater than some of the others observed by Swain and Scott and, in fact, the data on the relative reactivity of water, chloride and acetate toward chloroform can be fit by the equation of Edwards[13] with an α value of 1.77 and a β of 0.145. Each of these values is within the range found by Edwards for reactions that seem rather clearly to be SN2 in character.

In addition to reinvestigating part of the *p*H profile of the reaction we should like to comment briefly on one of the assumptions made by HTT in the deduction of their reaction mechanism.[4] They assumed that only one reaction mechanism operated over the entire *p*H range. While such an assumption has the advantage of simplicity compared to our proposal that there are two mechanisms for hydrolysis, our suggestion that chloroform hydrolyzes by some mixture of the SN1 and SN2 mechanisms at *p*H's below 5, just as numerous other halides have been shown to do, is, in another sense, simpler than a hypothesis of the operation of a new and different mechanism.

Experimental

Reagents and Apparatus.—The purification of chloroform has been described previously.[2] Some of the solutions in "oxygen-free" water were prepared from water that had been boiled and cooled under nitrogen. For other solutions the vapor space of the container was flushed with nitrogen and the solution shaken vigorously to equilibrate the dissolved gases with the separate gaseous phase, the cycle being repeated six times.

The constant temperature bath was a 5-l. flask in which water was refluxed (over boiling stones). The boiling action served to shake the floating reaction tubes gently.

Kinetic Runs.—In a typical run 0.20 ml. of chloroform (0.298 g.) was dissolved in 50 ml. of 0.0980 *M* acetic acid, 0.1031 *M* sodium acetate, 0.100 *M* sodium perchlorate in "oxygen-free" water. Three 5-ml. samples of this solution were titrated with standard alkali solution to the phenolphthalein end-point and six 5-ml. samples were placed in glass tubes of about 10-ml. capacity under nitrogen. Each tube was then frozen in a −80° bath, evacuated to about 8 mm. pressure and sealed. The tubes were then placed in the constant temperature bath and at intervals tubes were removed, opened and their contents rinsed into a flask for titration. In a number of cases, after the completion of the acidimetric titration the solutions were made slightly acidic with dilute perchloric acid and then titrated with silver nitrate using dichlorofluorescein as an indicator.

Calculation of Rate Constants.—From the change in acid concentration shown by titration the change in chloroform concentration was calculation from the relation

$$\Delta[CHCl_3] = \frac{\Delta[HA]}{3 + f}$$

where f is the fraction of the chloroform that produces formate upon hydrolysis (the rest gives carbon monoxide).[2] In some runs the value of f was calculated from chloride ion determinations that were made simultaneously with some of the acidimetric titrations. In all of the other runs the value (0.15) determined previously[3] for chloroform was used. The negative value (−0.28) found in the presence of 0.158 *M* formate may be significant, indicating that some of the formate is decomposed to carbon monoxide because of the formation of some formylated intermediate. In any event, the value of k is rather insensitive to the value of f used in calculating it and furthermore other facets of our present techniques make our rate constants considerably less accurate than those obtained in most of the earlier papers in this series.

Acknowledgments.—We are indebted to Dr. Kozo Tanabe for many beneficial discussions during the course of this work.

ATLANTA, GA.

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[11] J. Hine, R. Butterworth and P. B. Langford, THIS JOURNAL, **80**, 819 (1958).

[12] C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

[13] J. O. Edwards, *ibid.*, **76**, 1540 (1954).