TABLE IV

ADDITION OF CF_3 TO *trans*-DICHLOROETHYLENE AT 65°

In 2,3-Dimethylbutane

CF_3H/N_2	X_{Hydr}/X_{Substr}	k_2/k_1
0.499	No substr.	..
.510	No substr.	..
.507	No substr.	..
.276	3.51	2.90
.276	3.51	2.90
.274	3.51	2.95
.277	3.51	2.91
	Average	2.92

discussed by Lewis and Mayo,[16] who explained the low reactivity of diethyl maleate by its non-coplanarity.

TABLE V

THE RELATIVE RATE CONSTANTS (k_2) OF CF_3 RADICAL ADDITION AT 65° IN ISOÖCTANE

k_1 denotes the rate constant of the reaction CF_3 + isoöctane → CF_3H + isoöctyl radical

Substrate	No. of expt.	Range of X_{Hydr}/X_{Substr}	k_2/k_1
cis-Dichloroethylene	10	8–14	6.5 ± 0.6
trans-Dichloroethylene	14	5–132	12.5 ± .5
Trichloroethylene	5	2–13	12.8 ± .8
Tetrachloroethylene	4	0.3–2	1.3 ± .4
Diethyl maleate	12	17–92	26.7 ± 1.0
Diethyl fumarate	14	41–213	85 ± 6.0
Tetramethylethylene	10	190–960	538 ± 15

The electrophilic nature of CF_3 radicals is clearly demonstrated by the low reactivity of the dichloroethylenes and tetrachloroethylene which contrasts with the high reactivity of the butene-2's and tetramethylethylene. The presence of Cl atoms or CH_3 groups on the reactive center introduces a steric hindrance which reduces the rate of CF_3 addition to tetrachloroethylene or tetramethylethylene. In the former compound the polar effect reduces the reactivity even more, while in the latter the opposite polar effect more than compensates for the steric hindrance making tetramethylethylene slightly more reactive than ethylene.[1] It should be pointed out that the mesomeric effect of a Cl atom on the β-carbon enhances the reactivity of the olefin[17]; the k_2/k_1 for vinyl chloride was found to be 273 and for vinylidene dichloride 509. This effect explains the relative reactivity of trichloroethylene.

Finally, some photolytic experiments carried out in pure tetramethylethylene should be mentioned. The small amounts of CF_3H produced in such experiments were attributed to the reaction

$$CF_3 + (CH_3)_2C{=}C(CH_3)_2 \rightarrow CF_3H + \cdot CH_2(CH_3)C{=}C(CH_3)_2 \quad k_6$$

which competed with reaction 2. On the other hand C_2F_6 formed in such a process is believed to represent the result of the cage recombination of CF_3 radicals. The results of three experiments carried out at 65° led to the following average values for the respective ratios: $C_2F_6/N_2 = 0.204$ and $CF_3H/N_2 = 0.008$. Accepting the interpretation given above we deduce therefore that k_6/k_2 for tetramethylethylene is 0.005. Since $k_2/k_1 = 538$, it follows that $k_6/k_1 = 2.7$, *i.e.*, the rate constant k_6' of H abstraction from tetramethylethylene *per active H* is 0.23 of that of H abstraction from isoöctane. Similar experiments carried out in toluene and in mesitylene[3] led to k_6'/k_1 ratios of 0.12 and 0.14, respectively.

Acknowledgment.—We wish to thank the National Science Foundation and the Wright–Patterson Air Research and Development Command for financial support of this investigation.

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[16] F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1533 (1948).

[17] Unpublished results from this Laboratory.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.]

Kinetics of Proton Transfer in Methanol for a Series of Carboxylic Acids of Varying Strength

BY ERNEST GRUNWALD[1] AND S. MEIBOOM

RECEIVED JANUARY 9, 1963

It has been shown previously that in methanol containing benzoic acid and sodium benzoate, the rate of proton exchange in reactions involving these solutes is given at room temperature by: $R_M = k_1[HBz] + k_2[HBz][NaBz]$. The k_1-process was found to involve two methanol molecules and a cyclic reaction mechanism; the k_2-process was found to involve one methanol molecule. We now report n.m.r. measurements of k_1 and k_2 in methanol at 24.8° for a series of nitro-substituted benzoic acids in order to evaluate the sensitivity of these rate constants to acid strength. Values of pK_A, $10^{-5}k_1$ (sec.$^{-1}$) and $10^{-8}k_2$ (sec.$^{-1}$ M^{-1}) are, respectively: benzoic, 9.41, 1.31, 1.21; *m*-nitrobenzoic, 8.34, 3.6, 2.5; *p*-nitrobenzoic, 8.33, 4.5, 2.7; *o*-nitrobenzoic, 7.56, 19, 1.8; 3,5-dinitrobenzoic, 7.38, 16, 4.1. Except for *o*-nitrobenzoic acid, plots of log k_1 or log k_2 *vs.* log K_A are nicely linear, the slopes being 0.53 for log k_1 and 0.26 for log k_2. The low sensitivity to acid strength obtained for the termolecular process represented by k_2 is consistent with a concerted reaction mechanism. The peculiar sensitivity obtained for the cyclic process represented by k_1 is too high to be consistent with a simple model for a concerted mechanism and too low to be consistent with a simple model for a two-step process involving an intimate ion pair intermediate.

In a preceding paper[2] the kinetics of proton exchange in buffered solutions of benzoic acid and sodium benzoate was studied in detail, using the nuclear magnetic resonance (n.m.r.) technique. It was found that the exchange of the hydroxyl protons of the solvent is catalyzed not only by methyloxonium ion and methoxide ion, but also by the buffer components. That is to say, the quantity R_M, defined by eq. 1, is greater than zero.

$$R_M = R - (k_{MeOH_2^+}[MeOH_2^+] + k_{MeO^-}[MeO^-]) \quad (1)$$

In eq. 1, R is the experimentally measured rate of proton exchange, and the quantity which is subtracted from R is the previously established rate law for proton exchange in the absence of buffer.[3] Numerical values of the rate constants $k_{MeOH_2^+}$ and k_{MeO^-} are available from the previous investigation.[3]

For data obtained at 25°, an analysis of R_M as a function of the formal concentrations of benzoic acid [HA]

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[1] Alfred P. Sloan Fellow, 1960–1961.

[2] E. Grunwald, C. F. Jumper and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

[3] E. Grunwald, C. F. Jumper and S. Meiboom, *ibid.*, **84**, 4664 (1962).

and its sodium salt [NaA] has led to the rate law shown in eq. 2.

$$R_M = k_1[\text{HA}] + k_2[\text{HA}][\text{NaA}] \qquad (2)$$

The reaction represented by the k_1[HA] term was found to be second order in methanol and was shown to be a cyclic process. The reaction represented by the k_2[HA][NaA] term was found to be first order in methanol and was thought to be a concerted transfer of two protons by a termolecular push–pull mechanism.[4]

To provide further evidence concerning the mechanisms of these reactions, we now report measurements of the sensitivity of k_1 and k_2 to changes in the acid strength. We have used a series of nitro-substituted benzoic acids to cover a hundredfold variation in K_A. For the *m*- and *p*-substituted acids, plots of log k_1 and log k_2 *vs.* log K_A were nearly linear. The slopes, which measure the sensitivity of the rate constants to acid strength, were 0.53 for d log k_1/d log K_A, and 0.26 for d log k_2/d log K_A.

Results

The methods of measurement and design of the experiments can be treated very briefly here, since they are very similar to those described in detail for benzoic acid.[2] All measurements were made at 24.8°. The rate of exchange of the OH-protons was obtained from measurements of the shape or width of the n.m.r. signal due to the CH_3-protons of methanol.[3] In order to sort out the various kinetic terms contributing to the exchange, it was convenient to do the experiments in sets—each set consisting of a series of concentrations at constant acid–base ratio. Thus in each set the concentrations of methyloxonium ion and methoxide ion were constant (except for interionic effects), and the contributions of these ions to the total rate of exchange could be obtained for each set from the limiting value of R at zero concentration. It was therefore possible to analyze the results without requiring an independent value of K_A. In fact, the limiting values of R could be used to calculate K_A, once the rate constants $k_{\text{MeOH}_2^+}$ and k_{MeO^-} have been determined using a buffer of known K_A—as was done in reference 3.

It was found that eq. 2 applies to all acids investigated in this study. Values of the rate constants k_1 and k_2 were calculated by least-square methods, as described previously.[5] The results are shown in Table I. It is seen that for each acid, k_1 and k_2 are constant over a wide range of acid–base ratio, as required by the assumed law.[6]

Table I also lists pK_A values for the acids in methanol at 25°. For benzoic acid and the mononitrobenzoic acids, these values are averages based on concordant results obtained by conductometric[7] and colorimetric[8] methods, and we regard them as accurate to 10% or better. Our evaluation, in a previous paper,[3] of the rate constants $k_{\text{MeOH}_2^+}$ and k_{MeO^-} was based on these same values, and the smooth fit of our kinetic data to a single rate law, irrespective of the nature of the buffer acid, further confirms at least their relative accuracy.

TABLE I

VALUES OF k_1 AND k_2 FOR VARIOUS ACIDS IN METHANOL AT 24.8°

$\frac{[\text{HA}]}{[\text{NaA}]}$	pK_A	$k_1 \times 10^{-5}$, sec.$^{-1}$	$k_2 \times 10^{-8}$, sec.$^{-1}$ $M.^{-1}$
Benzoic acid[2]			
...	9.409	1.31	1.21
m-Nitrobenzoic acid			
2.18	8.344	3.7	2.7
0.273	8.344	3.5	2.4
	Av.	3.6	2.5
p-Nitrobenzoic acid			
2.19	8.326	4.7	2.8
0.310	8.326	4.2	2.6
	Av.	4.5	2.7
o-Nitrobenzoic acid			
1.98	7.556	18	2.0
0.122	7.556	17	2.25
0.0574	7.556	22	1.3
	Av.	19	1.8
3,5-Dinitrobenzoic acid			
1.57	7.377	17	3.5
0.241	7.377	15	4.7
	Av.	16	4.1

For 3,5-dinitrobenzoic acid, the only value reported has been obtained by a conductometric method.[7b] An independent check on this value would be desirable, and such a value can be obtained from our kinetic data. As mentioned above, extrapolation of the exchange rate to zero buffer concentration gives the exchange involving methyloxonium and methoxide ion. As the rate constants for these reactions are known, the concentrations of the ions, and hence K_A, can be obtained. In the actual calculations, the least-squares treatment[5] of the rates of exchange at each buffer ratio provides us with a value of the parameter α, defined by eq. 3, in which K_A is the only unknown

$$\alpha = k_{\text{MeOH}_2^+}K_A[\text{HA}]/[\text{A}^-] + k_{\text{MeO}^-}K_w[\text{A}^-]/K_A[\text{HA}] \quad (3)$$

Values of the other constants used in eq. 3 are, at 24.8°: $k_{\text{MeOH}_2^+} = 8.79 \times 10^{10}$ sec.$^{-1}$, $k_{\text{MeO}^-} = 1.85 \times 10^{10}$ sec.$^{-1}$, and $K_w = 1.21 \times 10^{-17}(M^2)$.[3,9] The average value of K_A for 3,5-dinitrobenzoic acid obtained in this way at two buffer ratios is $(4.2 \pm 0.2) \times 10^{-8}(M)$ at 24.8°. The previously reported conductometric value[7b] is $3.9 \times 10^{-8}(M)$, in good agreement.

According to the Hammett equation,[10] we expect plots of log k_1 or log k_2 *vs.* log K_A to be linear for the *m*- and *p*-substituted acids, the slope being a quantitative measure of the sensitivity of these rate constants to changes in acid strength. As a matter of fact, the data for the acids except *o*-nitrobenzoic acid are represented within their experimental error by the empirical eq. 4 and 5. The value of r shown in these equations is the standard error of fit.

$$\log k_1 = 10.09 + 0.533 \log K_A;\ r = 0.05 \qquad (4)$$

$$\log k_2 = 10.58 + 0.263 \log K_A;\ r = 0.03 \qquad (5)$$

Log–log plots of the data are shown in Fig. 1 and 2. The point for *o*-nitrobenzoic acid is seen to deviate.

Discussion

k_2-Term.—If the process measured by the k_2-term is indeed a concerted push–pull process, we expect k_2 to be

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(4) (a) C. G. Swain and M. M. Labes, *J. Am. Chem. Soc.*, **79**, 1084 (1957); (b) C. G. Swain, J. T. McKnight and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

(5) The calculations utilized eq. 13 to 16 of ref. 2.

(6) While our results indicate that in *methanol*, both terms in eq. 2 continue to make significant contributions to R_M even when K_A is increased a hundredfold, Feldbauer and Weller report that in *ethanol*, the k_1 term is insignificant for acetic acid (pK_A 10.3 in ethanol) and the k_2 term is insignificant for formic acid (pK_A 9.2); H. Feldbauer and A. Weller, *Z. physik. Chem.* (Frankfurt), **32**, 263 (1962).

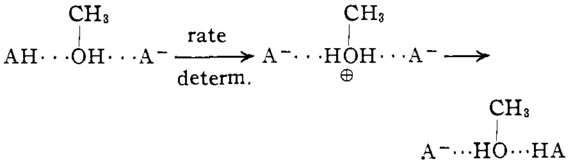
(7) (a) H. Goldschmidt and E. Mathiesen, *Z. physik. Chem.*, **119**, 452 (1926); (b) H. Goldschmidt and C. F. Aas, *ibid.*, **112**, 423 (1924).

(8) (a) M. Kilpatrick and C. A. Arenberg, *J. Am. Chem. Soc.*, **75**, 3812 (1953); (b) M. Kilpatrick and W. H. Mears, *ibid.*, **62**, 3047 (1940); (c) I. M. Kolthoff and L. S. Guss, *ibid.*, **61**, 330 (1939); **62**, 1494 (1940).

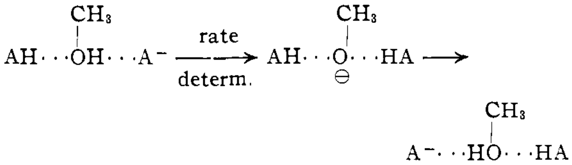
(9) J. Koskikallio, *Suomen Kemi.*, **30B**, 111, 155 (1957).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

quite insensitive to K_A. This is because the effect of an increase in the acid strength of HA on the rate tends to be counterbalanced by the effect of the concomitant decrease in the base strength of A^-. On the other hand, if the process were not concerted, we would expect k_2 to increase markedly with K_A if the rate-determining step were the acid ionization of HA (eq. 6), and to decrease markedly if it were the base ionization of A^- (eq. 7).



$$\mathrm{AH\cdots \overset{CH_3}{OH}\cdots A^-} \xrightarrow[\text{determ.}]{\text{rate}} \mathrm{A^-\cdots H\overset{CH_3}{\underset{\oplus}{O}}H\cdots A^-} \longrightarrow \mathrm{A^-\cdots H\overset{CH_3}{O}\cdots HA} \quad (6)$$



$$\mathrm{AH\cdots \overset{CH_3}{OH}\cdots A^-} \xrightarrow[\text{determ.}]{\text{rate}} \mathrm{AH\cdots \overset{CH_3}{\underset{\ominus}{O}}\cdots HA} \longrightarrow \mathrm{A^-\cdots H\overset{CH_3}{O}\cdots HA} \quad (7)$$

According to either mechanism 6 or 7 we would predict a linear dependence of log k_2 on log K_A not only from the Hammett relationship, but also because the Brönsted catalytic law would apply. The slopes of Brönsted catalytic plots can be predicted by means of the plausible treatment given by Leffler.[11] According to this treatment, the slope is a measure of the "degree of resemblance" of the transition state to reagents and products. The treatment implies[12] that the slope is equal to $(v_{\ddagger} - v_{\text{reagent}})/(v_{\text{product}} - v_{\text{reagent}})$, where v is a variable characteristic of the reactive functional group. In the present case, v is almost certainly an electrical parameter such as the amount of negative charge on the carboxyl group.

In both 6 and 7 the transition state for the rate-determining step may be expected to resemble the reaction intermediate since the latter is relatively unstable.[13] Hence for the acid-catalyzed reaction 6, the slope of log k_2 *vs.* log K_A is expected to be near $+1$, while for the base-catalyzed reaction 7 it is expected to be near -1. Compared to these values the experimental slope is very small, thus supporting our previous conclusion[2] that we are dealing with a push–pull mechanism. However, the fact that the slope *is* slightly positive suggests that in the transition state there is a partial negative charge on the carboxyl group and, hence, a partial positive charge on the oxygen atom of methanol. Similar evidence for a partial positive charge on the central atom in a concerted displacement reaction has also been obtained for the S_N2 reactions of carbon compounds.[14]

In Fig. 2 the point for *o*-nitrobenzoic acid deviates from the log–log plot of the data for the other acids. We can, however, account for this deviation if we are willing to make some relatively mild assumptions about the symmetry of the various benzoate anions. We shall assume that the two oxygen atoms in the carboxylate group are equivalent, except for *o*-nitrobenzoate where interaction with the adjacent nitro group destroys the equivalence.

We may now represent each K_A and k_2 as the product of a chemical factor and a statistical factor[15] as in eq. 8, where the σ's are symmetry numbers.

$$\begin{aligned} K_A &= K_{A,\text{chem}} \times \sigma_{HA}/\sigma_{A^-}\sigma_{H^+} \\ k_2 &= k_{2,\text{chem}} \times \sigma_{HA}\sigma_{A^-}/\sigma^{\ddagger} \end{aligned} \quad (8)$$

A more fundamental extrathermodynamic relationship than that between k_2 and K_A is that between $k_{2,\text{chem}}$ and $K_{A,\text{chem}}$, eq. 9.

$$\log k_{2,\text{chem}} = S \times \log K_{A,\text{chem}} + b \quad (9)$$

The quantities S and b in eq. 9 are parameters. Upon substituting from eq. 8 we obtain eq. 10.

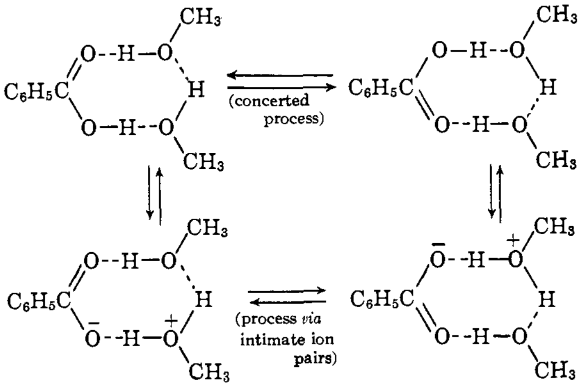
$$\log k_2 = S \log K_A - (S - 1) \log \sigma_{HA} + (S + 1) \log \sigma_{A^-} + S \log \sigma_{H^+} - \log \sigma^{\ddagger} + b \quad (10)$$

The symmetry numbers σ_{HA}, σ_{H^+} and $\sigma^{\ddagger}$ are very probably constant throughout the series; $\sigma_{A^-} = 2$ except for *o*-nitrobenzoate where it is unity, by hypothesis. Absorbing all the constant terms into a single number, we may rewrite eq. 5 in the form

$$\log k_2 = 0.263 \log K_A + 1.263 \log \sigma_{A^-} + 10.20 \quad (11)$$

Applying this equation to *o*-nitrobenzoic acid, we predict that $k_2 = 1.64 \times 10^8$ sec.$^{-1}$ M^{-1}, in good agreement with the experimental value of $(1.8 \pm 0.4) \times 10^8$.

k_1-Term.—The relationship between the reaction mechanism and the slope of the Hammett–Brönsted plot for the k_1-term should be similar to that for the k_2-term. The question again is whether the proton exchange is a concerted process, as in 12a, or whether it proceeds by a stepwise mechanism, perhaps by way of intimate ion pairs as in 12b.



(12a)

(12b)

It is helpful to consider two extreme, somewhat idealized models: (1) a concerted process with very little charge development in the transition state; (2) an ion-pair mechanism with nearly complete charge development in the transition state. In case 1 we expect the rate to be almost independent of the acid strength, since the effect of an increase in the acid strength of the COOH protons tends to be canceled by the effect of the nearly equal decrease in the base strength of the carbonyl oxygen. (The Hammett ρ-value for the protonation of benzoic acids with "well behaved" substituents is -1.09.[16]) On the other hand, in case 2, which represents the other extreme, we expect the slope to be only slightly less than unity.

Unfortunately, the experimental value of the slope, 0.53, does not agree with either of these models. Instead, it appears that the actual charge development in the transition state is neither very small nor almost complete. The experimental result therefore does not distinguish between the alternative mechanisms and, in fact, it cannot be reconciled with either mechanism without subjecting our prior notions concerning these mechanisms to some strain.

The discussion up to this point has neglected the fact that the exchange can take place only in that sub-

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(11) J. E. Leffler, *Science*, **117**, 340 (1953).

(12) J. E. Leffler and E. Grunwald, "The Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter VI.

(13) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(14) See, for example, S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(15) S. W. Benson, *ibid.*, **80**, 5151 (1958).

(16) R. Stewart and K. Yates, *ibid.*, **82**, 4059 (1960).

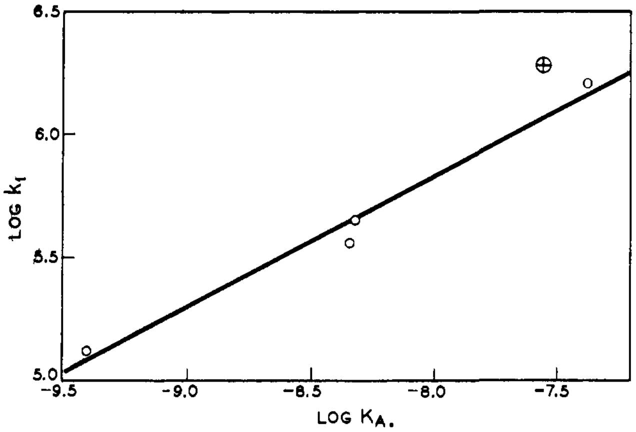
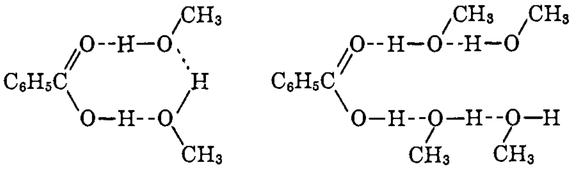


Fig. 1.—log k_1 *vs.* log K_A for nitro-substituted benzoic acids in methanol at 25°. The point indicated by the cross is for *o*-nitrobenzoic acid and has been disregarded in drawing the straight line.

species of the acid in which a suitable cyclic hydrogen-bonded pathway is present in the solvation shell of the carboxyl group; see eq. 13.



(13)

(can react by the k_1-process) (cannot react by the k_1-process)

If we denote the fraction of this subspecies by *f*, then the formal rate constant k_1 is related to a chemical rate constant $k_{1,\text{chem}}$ by eq. 14, where σ is the appropriate statistical factor.[17]

$$k_1 = \sigma f k_{1,\text{chem}} \qquad (14)$$

To form some opinion as to the probable magnitude of *f* for various acids, it is instructive to consider the following (molar) association constants for hydrogen-bonded complexes in carbon tetrachloride at 25°: acetic acid–ethanol,[18] *ca.* 100; ethanol–ethanol,[19] 0.64; ethanol–ethyl acetate,[19] 1.7 (the hydrogen bond is to the carbonyl group). We note that the association constant for the formation of $CH_3COOH \cdots OHCH_2CH_3$ is large. On the other hand, the association constant for the formation of $CH_3CH_2OH \cdots OCOEt{\cdot}CH_3$ is only somewhat greater than that for the formation of the ethanol dimer. Extrapolating these results to the solvation of acetic acid in ethanol, we predict that virtually every carboxyl proton is hydrogen bonded to a solvent molecule. On the other hand, it is by no means certain that virtually every carbonyl oxygen atom is hydrogen bonded to an ethanol molecule.

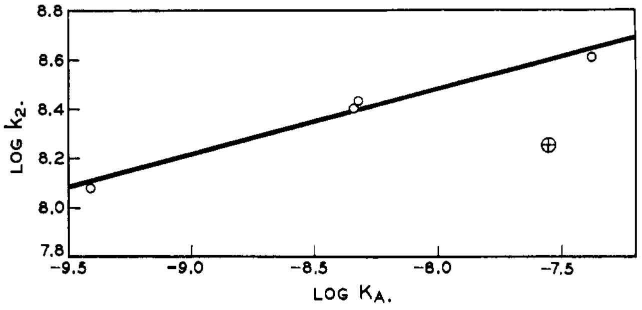


Fig. 2.—log k_2 *vs.* log K_A for nitro-substituted benzoic acids. For explanation, see caption of Fig. 1.

If we now consider a series of acids that are stronger than acetic acid, we expect that the solvation of the carbonyl oxygen atom becomes progressively less complete as the acid strength increases, while that of the carboxyl proton continues to be virtually complete. This picture should apply also to the series of nitrobenzoic acids in methanol considered in the present investigation. We therefore expect that *f* will decrease with increasing acid strength. It should be emphasized that the decrease in *f* is due to a decrease in the total fraction of bifunctionally solvated subspecies; the distribution of the bifunctionally solvated subspecies into cyclic and non-cyclic isomers (eq. 13) could remain quite constant.

For purposes of elucidating the reaction mechanism, we are interested in the variation of $k_{1,\text{chem}}$ (eq. 14) with K_A. Since *f* is expected to decrease with increasing K_A, the slope, 0.53, of the plot of log k_1 *vs.* log K_A in Fig. 1 sets a lower bound to the slope of log $k_{1,\text{chem}}$ *vs.* log K_A.[20] While we cannot give a quantitative estimate of the difference, it is in such a direction as to make the ion-pair mechanism somewhat more probable than the concerted mechanism.

The value of k_1 for *o*-nitrobenzoic acid is almost double the value predicted from eq. 4. While any interpretation of the discrepancy at this stage is only a guess, we believe that the solvation of the *o*-nitro group may be providing additional cyclic pathways along which proton transfer can take place.

Experimental

The preparation of pure methanol and of the mononitrobenzoic acids has been described previously.[3] 3,5-Dinitrobenzoic acid was a reagent-grade commercial sample and was twice recrystallized from pure boiling water and dried *in vacuo* over P_2O_5; m.p. 208.5–209.0° (cor.). Buffer solutions were prepared and rates measured as described previously for benzoic acid.[2]

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(17) Equation 14 applies only if the interconversion of the various solvated subspecies is fast compared to the proton exchange.

(18) W. C. Coburn, Jr., Ph.D. Thesis, Florida State University, Tallahassee, Fla., 1954; value estimated from the effect of acetic acid on the rate of reaction between acetic anhydride and ethanol.

(19) (a) W. C. Coburn, Jr., and E. Grunwald, *J. Am. Chem. Soc.*, **80**, 1318 (1958); (b) E. Grunwald and W. C. Coburn, Jr., *ibid.*, **80**, 1322 (1958).

(20) As long as the log–log plot is smooth we need not consider the effect of statistical factors, because changes in statistical factors would be discontinuous and cause discrete deviations from the line.