Kinetics of Proton Transfer in Methanol Solutions of Benzoic Acid and Sodium Benzoate

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This paper reports n.m.r. measurements of the rate of proton transfer in methanol containing benzoic acid–sodium benzoate buffer. The kinetic analysis showed that, in addition to the processes involving methyloxonium ion and methoxide ion, two distinct processes involving the buffer are present at room temperature. The rate of proton exchange in the latter processes is given by $R_M = k_1[HBz] + k_2[HBz][Bz^-]$, with $k_1 = 1.3 \times 10^5$ sec.$^{-1}$ and $k_2 = 1.2 \times 10^8$ sec.$^{-1} M^{-1}$ at 24.8°. The number of methanol molecules involved in these processes can be obtained from a comparison of the rate as deduced from the methyl resonance with that obtained from the combined carboxyl–hydroxyl resonance. The k_1 process was found to involve two methanol molecules. The rate constant k_1 is much larger than the maximum possible rate constant for acid dissociation and represents a cyclic process. The k_2 process was found to involve one methanol molecule. Rate measurements were also made at −81.6°. In addition to the k_1 and k_2 terms, a third term, $k_3[HBz]^{1/2}[Bz^-]^{1/2}$, appears in the kinetic analysis. The values of the rate constants are: $k_1 = 2.2 \times 10^2$ sec.$^{-1}$, $k_2 = 1.7 \times 10^6$ sec.$^{-1} M^{-1}$ and $k_3 = 1.1 \times 10^4$ sec.$^{-1}$ at −81.6°. The k_3 term is polymolecular in methanol and the mechanism by which it arises is not understood. Some conductivity measurements of KCl in methanol showed that this salt behaves as a strong electrolyte at −78.8°. We therefore infer that ionic association of sodium benzoate is not extensive at −81.6°.

Proton transfer reactions in water and in the alcohol solvents are noted for their conspicuous dependence on detailed microscopic properties of the solvent. For example, the thermodynamic quantities for acid and base dissociation indicate by their very complexity [2–5] that this process depends not only on the acid–base properties of the solvent molecules but also on the nature of their quasi-crystalline arrangement.[5] In the field of kinetics, proton transfer from an acid such as hydronium ion or R_3NH^+ to a base such as hydroxide ion, acetate ion or an amine, proceeds readily by mechanisms involving one or several intervening solvent molecules,[6–10] and therefore depends intimately on details of solvation.

Nuclear magnetic resonance provides a unique tool for studying the role of the solvent in proton transfer rate processes. Under suitable conditions it is possible to measure the rate of proton exchange both on the solvent molecules and on the solute molecules. By comparing these two rates it is possible to draw conclusions as to the number of solvent molecules involved in each kinetic process.

We here report such a kinetic study of proton transfer between methanol and the components of benzoic acid–sodium benzoate buffers in dilute solution in methanol. Our results establish that one mechanism for proton transfer from benzoic acid to benzoate ion is a thermolecular process involving one methanol molecule. Another process, which does not involve the benzoate ion, is first order in benzoic acid and involves two methanol molecules. The rate of this process is much greater than that of acid dissociation and a cyclic mechanism is indicated. At low temperatures an additional kinetic term appears in which the rate is one-half order each in benzoic acid and benzoate ion. The mechanism associated with this term is not understood at present.

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Method of Rate Calculation

In the systems studied, proton exchange can take place between methanol and (i) $CH_3OH_2^+$, (ii) CH_3O^- and (iii) the buffer components. The results for the rate constants for reactions i and ii were reported in a previous paper.[11] The rate constants are so high that only solutions with very low methyloxonium and methoxide concentrations can be employed in the rate determinations, and the lifetime of the methyloxonium ion is too low to be observable as a separate line, or even to contribute measurably to the hydroxyl line width.

On the other hand, the rate of exchange between benzoic acid and methanol is slow enough to contribute a measurable broadening of the OH resonance, provided the benzoate concentration is low. And at low temperatures (about −80°) the carboxyl protons could be observed directly. By comparing the OH proton exchange rate, as determined from the CH_3 resonance, with the exchange rate between methanol and benzoic acid, as obtained from the carboxyl or from the coalesced carboxyl–hydroxyl resonance, it is possible to determine the number of methanol molecules involved in each kinetic process.

In the following we shall use the symbol R_M to denote that portion of the OH proton exchange rate of methanol which is due to reaction with the buffer components. We obtain R_M from the equation

$$R_M = R - R_i - R_{ii}$$

where R is the total rate of OH proton exchange of methanol, as obtained from the CH_3 resonance, and R_i and R_{ii} are the rates of proton exchange between methanol and (i) methyloxonium ion and (ii) methoxide ion, respectively. Since the rate constants for the latter two reactions are known,[11] R_i and R_{ii} can be calculated for any given solution.

The rate at which the protons of the carboxyl group exchange with the OH group of methanol will be denoted by R_C. The rate R_C is obtained from the carboxyl resonance or from the coalesced carboxyl–hydroxyl resonance, as described in detailed below. The ratio R_M/R_C is equal to the average number of methanol protons that exchange each time a carboxyl proton exchanges.

CH$_3$-Protons.—N.m.r. measurements and rate calculations were done as described previously.[11]

Separate COOH Line.—At low temperatures and low benzoate concentrations the rate of exchange of benzoic acid was slow enough so that the n.m.r. line

(11) E. Grunwald, C. F. Jumper and S. Meiboom, J. Am. Chem. Soc., 84, 4664 (1962).

Table I

Experimental Test of Equation 5 for Very Dilute Buffer Solutions of p-Nitrobenzoic Acid at 24.8°

$P_C \times 10^4$	$(1/T_2' - 1/T_2)_{Me}$ obsd.	r_1, sec.	$B(O^{17})$ (eq. 4)	$3(1/T_2' - 1/T_2)_{Me}$ $+ B(O^{17})$	$(1/T_2' - \langle 1/T_2 \rangle)_{OH}$ obsd.
2.2	0.433 ± 0.01	9.3×10^{-4}	0.113	1.41 ± 0.03	1.35 ± 0.07
1.1	1.001 ± 0.02	3.06×10^{-3}	0.070	3.07 ± 0.06	3.23 ± 0.18

due to the carboxyl protons could be observed directly. In this case the measurement of line width gave a direct measurement of R_C

$$\frac{1}{T_2'} = \frac{1}{T_2} + \frac{R_C}{[HBz]} \qquad (1)$$

In eq. 1 and in subsequent equations, $1/T_2'$ is used to denote one-half of the line width at half height, in radians per sec.; $1/T_2$ is the corresponding quantity in the hypothetical case of zero exchange. We have assumed that $1/T_2 = 1/T_1$, and have evaluated the latter from rf saturation experiments on the exchange-broadened lines. At $-81.6°$, the value of $1/T_1$ for air-saturated solutions was 4 sec.$^{-1}$, which was less than 4% of the smallest observed value of $1/T_2'$.

Coalesced OH–COOH Line.—At high exchange rates a separate COOH line is no longer observed. In this case R_C can be determined from the width of the coalesced OH–COOH line. This line results from two distinct averaging processes: (a) transfers between the individual components of the OH quadruplet, with a rate characterized by an average lifetime τ_1 given by[12] $1/\tau_1 = R/[MeOH]$; and (b) transfers between the COOH frequency and the average frequency of the protons, the rate of which can be characterized either by the average residence time τ_2 of a proton on the COOH group or by the average residence time τ_2' of a proton on the OH group. These quantities are related to R_C by the equations, $R_C = [HBz]/\tau_2 = [MeOH]/\tau_2' = ([HBz] + [MeOH])/(\tau_2 + \tau_2')$.

A rigorous derivation of an expression for the line width is quite complicated and hardly worthwhile. However, for the case of fast exchange, i.e., $1/\tau_1 \gg J$, and if $\delta \gg J$, the contributions to the width of the collapsed line from the two processes a and b can be taken as additive. In this approximation the observed width, expressed as a relaxation time T_2', becomes

$$(1/T_2' - \langle 1/T_2 \rangle)_{OH} = P_M{}^2 P_C{}^2 \delta^2 (\tau_2 + \tau_2') +$$
$$P_M \frac{3J^2 \tau_1}{4}\left(1 + \frac{1}{1 + \tau_1{}^2\delta^2}\right) \qquad (2)$$

where

$P_M = [MeOH]/([MeOH] + [HBz])$
$P_C = 1 - P_M$
$J = $ the coupling constant (in radians per sec.) of CH_3 and OH protons
$\delta = $ the chemical shift (in radians per sec.) of COOH vs. OH protons
$\langle 1/T_2 \rangle = P_M(1/T_2)_{OH} + P_C(1/T_2)_{COOH}$, a weighted average for the two kinds of protons

The factor $3J^2/4$ is the second moment of the OH quadruplet.[13]

The value of $(\tau_2 + \tau_2')$ and hence R_C can be obtained from the measured value of $(1/T_2' - \langle 1/T_2 \rangle)_{OH}$, since the last term on the right in eq. 2 can be evaluated from the broadening of the CH_3 resonance. This is easily done because it will be noted that this term is just three times the observed broadening of the CH_3 line,[14] which we shall write as $(1/T_2' - 1/T_2)_{Me}$. Equation 2 can therefore be cast in the form

(12) In a strict analysis the contribution to $1/\tau_1$ from spontaneous spin inversion of the CH_3 protons must be added to the equation, as was done in a similar case in ref. 11. This correction is of the order of $1/T_1$ of the methyl protons, and can be neglected here.
quadruplet and the CH_3 doublet.
(13) L. H. Piette and W. A. Anderson, J. Chem. Phys., **30**, 899 (1959).
(14) The factor 3 is just the ratio of the second moments for the OH–

$$(1/T_2' - \langle 1/T_2 \rangle)_{OH} = 3P_M(1/T_2' - 1/T_2)_{Me} +$$
$$P_M{}^2 P_C{}^2 \delta^2 \frac{[HBz] + [MeOH]}{R_C} \qquad (3)$$

In deriving eq. 3, satellite lines due to the isotopes C^{13} (natural abundance 1%) and O^{17} (natural abundance 0.037%) have been neglected. The spin–spin interaction between C^{13} and the OH proton is probably less than 10 c.p.s.[15,16] and their contribution to the line width can be neglected. However, the interaction between O^{17} and the hydroxyl proton is much larger and can be a source of significant line broadening.[17]

In the notation of ref. 17 and for normal isotopic abundance, the additional broadening is given by

$$B(O^{17}) = \frac{3.7}{3} \times 10^{-4} \tau_1 \sum_n \frac{n^2(J_{eff})^2}{1 + (nJ_{eff}\tau_1)^2} \qquad (4)$$

where

$$n = {}^1/_2,\, {}^3/_2,\, {}^5/_2$$
$$J_{eff} = J'[T^1/(T^1 + \tau_1)]$$

The coupling constant J' for the O^{17}–H interaction in methanol is probably very similar to that for water, 580 radians per sec.,[17] and this value was used. The T^1 relaxation time of O^{17} in methanol was measured at 25° and found to be 0.0033 sec. Using these constants and typical experimental values of τ_1 from the broadening of the CH_3 resonance, the O^{17} broadening was found to be of the order of a few hundredths (sec.$^{-1}$) and was therefore significant at 25°. At $-81.6°$, where T^1 is almost certainly less than 0.001 sec., the O^{17} broadening could be neglected.

Allowing for this correction, the final equation used in calculating R_C becomes[18]

$$(1/T_2' - \langle 1/T_2 \rangle)_{OH} = 3P_M(1/T_2' - 1/T_2)_{Me} +$$
$$P_M{}^2 P_C{}^2 \delta^2 \frac{[HBz] + [MeOH]}{R_C} + B(O^{17}) \qquad (5)$$

A partial check as to the correctness of eq. 5 and the accuracy of our measurements is given in Table I. This table gives the results for two solutions in which P_C is so small that the term involving R_C is negligible. The only unknown remaining in eq. 5 is the chemical shift δ between OH and COOH protons. At low temperatures this quantity could be measured directly, since it was possible to find conditions under which the OH and COOH lines are separate. Above $-50°$, however, it was not possible to find any conditions under which this was so, and δ has to be estimated by an indirect approach. We measured δ', the chemical shift (in radians per sec.) between the CH_3 line and the coalesced OH–COOH line.

We write then

$$\delta' = (1 - P_C)\delta_{OH-CH_3} + P_C\delta_{COOH-CH_3} \qquad (6)$$

In principle, both δ_{OH-CH_3} and $\delta_{COOH-CH_3}$ are functions of P_C. However, since P_C is small, we may neglect the variation in $\delta_{COOH-CH_3}$ and assume that δ_{OH-CH_3} varies linearly with P_C.

$$\delta_{OH-CH_3} = \delta°_{OH-CH_3} + iP_C \qquad (7)$$

(15) D. R. McAdams, J. Chem. Phys., **36**, 1948 (1962).
(16) This is consistent with our failure to observe C^{14} satellites of the OH resonance at $-80°$, where exchange can be made very slow. The satellites are no doubt masked by the quadruplet structure.
(17) S. Meiboom, J. Chem. Phys., **34**, 375 (1961).
(18) In eq. 5 it is assumed that the same measure of O^{17} broadening applies to the carboxyl group as to the OH group. Whether this is true or not is only of academic interest, as $P_C \ll 1$ in all cases.

The quantities $\delta^\circ_{OH-CH_3}$ and i in eq. 7 are functions of the temperature. Combining eq. 6 and 7 and neglecting terms in P_C^2, we obtain

$$\delta' = \delta^\circ_{OH-CH_3} + (\delta + i)P_C \qquad (8)$$

In agreement with eq. 8, at 25°, δ' varies linearly with P_C up to at least 0.6 M benzoic acid. To obtain the chemical shift δ from the slope, we have estimated the parameter i by a method of comparison with the structurally similar model substance, benzamide. The N–H protons of benzamide exchange with methanol sufficiently slowly so that the value of the analogous parameter $i_{benzamide}$ can be measured directly at 25°.

The relevant data are shown in Table II. It is seen that at −81.6° the experimentally determined i-values for benzoic acid and for benzamide are nearly equal. This is probably no accident, in view of the similarity of the molecular structures, and the assumption seems justified that the i-values for benzoic acid and benzamide are also nearly equal to 25°. Since the latter is seen to be small, we have interpreted the slope of the plot of δ' vs. P_C on the basis that $i = 0$ for benzoic acid at 25°. The resulting estimate of δ might, because of the need for this assumption, be in error by as much as $+10\%$. Since R_C is proportional to δ^2, the corresponding error in R_C might be as much as $+20\%$.

TABLE II
EVALUATION OF THE CHEMICAL SHIFT δ FOR SOLUTIONS OF BENZOIC ACID IN METHANOL

Temp., °C.	δ, radians/sec.	$(\delta + i)$, radians/sec.	$i_{benzamide}$, radians/sec.
−100.3	2800 ± 30	—	—
−81.6	2790 ± 30	3440 ± 100	500 ± 100
−60.3	2650 ± 150	—	—
−50	—	—	450 ± 100
−20	—	—	380 ± 100
24.8	$(3120)^a$	3120 ± 30	30 ± 100

^{a} Estimated from $\delta + i$, assuming $i \approx 0$.

T_1 and T_2.—In the calculation of R from the n.m.r. spectrum of the CH$_3$ protons we need the value of T_1 for the OH protons, and in all rate calculations we need the value of T_2 for the particular line we are studying. Both of these quantities are functions of the benzoic acid concentration. At moderate concentrations (less than $\sim 1\ M$), we assume that the relationships are linear and write

$$1/T_1 = (1/T_1)_0 + m[HBz] \qquad (9)$$
$$1/T_2 = (1/T_2)_{reference} + m[HBz] \qquad (10)$$

In these equations, $(1/T_1)_0$ is the value for the particular protons in the pure solvent, $(1/T_2)_{reference}$ is the value measured for a reference solution consisting of $\sim$0.04 M HCl in methanol under identical conditions to those used for the benzoic acid solution, and m is a parameter characteristic of the particular protons and the temperature. In 0.04 M HCl, R is so large that exchange broadening is negligible. At −81.6°, m was evaluated from direct measurements of T_1 and $(T_1)_0$.[19] At 24.8°, m was evaluated from T_2 measurements under conditions where R and R_C were very large. The results are: For the OH protons, $m = 0.14$ at 24.8° and 1.36 at −81.6°; for the CH$_3$ protons, $m = 0.00$ at 24.8° and 0.52 at −81.6°.

Kinetic Analysis

Data at 24.8°.—From the data for the CH$_3$ protons we obtain the rate, R, which may be written as in equation 11

$$R = k_{MeOH_2^+}[MeOH_2^+] + \frac{k_{MeO^-}K_w}{[MeOH_2^+]} + R_M \qquad (11)$$

(19) Values of $(T_1)_0$ and experimental details are given in ref. 11.

TABLE III
KINETIC ANALYSIS OF THE EXCHANGE RATES R, BASED ON THE N.M.R. SPECTRUM OF THE CH$_3$ PROTONS. SOLUTIONS OF BENZOIC ACID AND SODIUM BENZOATE IN METHANOL, 24.8°

$\left(\dfrac{[HBz]}{[NaBz]}\right)$	Range of $10^3\ [HBz]$	$10^{-5}\ k_1$, sec.$^{-1}$	$10^{-8}\ k_2$, sec.$^{-1}\ M.^{-1}$
22.7	0.4–17	1.31	0.9$_3$
9.45	.3–2.0	1.31	$(1.2)^a$
4.10	.2–1.8	1.35	$(1.2)^a$
3.32	.06–23	1.30	1.3$_5$
2.31	.2–1.4	1.29	$(1.2)^a$
1.25	.05–22	$(1.3)^a$	1.4$_1$
0.204	.1–1.5	$(1.3)^a$	1.1$_6$

^{a} In some series the concentration range was too narrow to permit a sufficiently accurate determination of k_1 or k_2. In these cases only two free parameters were used in the least-squares treatment. The third parameter (indicated by parentheses in the table) was then taken as the average obtained in other series.

The values of the rate constants $k_{MeOH_2^+}$ and k_{MeO^-} have been reported in a preceding paper.[11] In the present work we wish to give a kinetic analysis of R_M, the rate of proton exchange of methanol due to reactions with benzoic acid and benzoate ion. Our procedure was to do several series of experiments at constant buffer ratio [HBz]/[NaBz] but variable buffer concentration. Neglecting interionic effects for the moment, the first two terms in (11) are constant in a given series. It was found that the concentration dependence of R_M can be represented accurately by eq. 12.

$$R_M = k_1[HBz] + k_2[HBz][NaBz] \qquad (12)$$

Equation 12 fits the data in any given series over a wide range in buffer concentration, and the same values of k_1 and k_2 will describe different series for more than a hundred-fold variation in the buffer ratio.

In our final calculations we made allowance for interionic effects by calculating molar activity coefficients, y, for all solutes and transition states from eq. 13, where z is the charge number of the solute and μ the ionic strength.

$$\log y = -1.89 z^2 \mu^{1/2}/(1 + 2.55\mu^{1/2}) \text{ at } 24.8° \qquad (13)$$

The numerical coefficients in this equation are appropriate for methanol at 24.8°, and the coefficient, 2.55, in the denominator is based on the further assumption of a uniform distance-of-closest-approach parameter of 5 Å. In our experiments, μ ranged up to 0.01 M.

The result of this treatment is that R is given by eq. 14

$$R = \alpha\xi + k_1[HBz] + k_2[HBz][NaBz] \qquad (14)$$

where α is independent of the ionic strength and is defined in eq. 15, while ξ varies with the ionic strength and is defined in eq. 16.

$$\alpha = k_{MeOH_2^+}K_A[HBz]/[Bz^-] + k_{MeO^-}K_w[Bz^-]K_A[HBz] \qquad (15)$$
$$\xi = 1 + (y^{-2} - 1)/\{1 + k_{MeO^-}K_w[Bz^-]^2/k_{MeOH_2^+}K_A^2[HBz]^2\} \qquad (16)$$

Here K_A is the acid dissociation constant of benzoic acid and K_w the autoprotolysis constant of methanol. In our experiments ξ was usually close to 1, but in a few cases it was as large as 2. The parameters α, k_1 and k_2 were calculated for each series (i.e., for each constant value of the buffer ratio) by a method of weighted least squares. The values of α obtained in this way were in each case consistent with the rate constants reported in the preceding paper,[11] the latter having been obtained by simple graphical extrapolation using low buffer concentrations only. It is seen in Table III that the values of k_1 and k_2 are remarkably constant over a wide range in buffer ratio. Our kinetic analysis

TABLE IV

EXCHANGE RATES, R_C, BASED ON THE COALESCED N.M.R. LINE OF THE OH AND COOH PROTONS. SOLUTIONS OF BENZOIC ACID AND SODIUM BENZOATE IN METHANOL, 24.8°

[HBz]	[NaBz]	$(1/T_2' -$ $(1/T_2))_{OH}$	$(1/T_2' - 1/T_2)_{Me}$	$B(O^{17})$	$R_C \times 10^{-5}$, M. sec.$^{-1a}$	$R_C \times 10^{-5}$, calcd.^{b}
0.400	0.00148	0.821	0.079	0.057	1.23	1.18
.274	.00101	.987	.126	.083	0.58	0.61
.393	.00310	.511	.064	.040	2.23	2.13
.270	.00213	.623	.088	.066	0.98	1.06

^{a} δ = 3120 radians per sec. ^{b} R_C = 0.71 × 10^5[HBz] + 1.52 × 10^8[HBz][NaBz].

gives no evidence of a first-order kinetic term proportional to the benzoate concentration.

Our results at 24.8° for the rate of exchange of the carboxyl protons with methanol, R_C, are summarized in Table IV. The kinetic analysis of R_C is simpler than that of R because kinetic terms involving exchange of methyloxonium ion and methoxide ion with methanol do not appear. As a matter of fact, the data are fitted satisfactorily by the empirical equation

$$R_C = k_1'[HBz] + k_2'[HBz][NaBz] \qquad (17)$$

where k_1' = 0.71 × 10^5 and k_2' = 1.52 × 10^8.

Although eq. 17 is based on data for only four solutions, its correctness has been confirmed by the close agreement of the values of k_1' with those obtained from solutions containing benzoic acid and HCl.[20]

Kinetic Order with Respect to Methanol at 24.8°.— As pointed out previously R_M is the rate of proton exchange on the OH group of methanol due to reaction with the buffer components; R_C is the rate of proton exchange between the COOH group of benzoic acid and the OH group of methanol. Both R_M and R_C are given by rate laws of identical form, namely eq. 12 and 17. If we assume that kinetic terms with identical concentration dependence in the two equations correspond to the same kinetic process, the ratio of their rate constants is equal to the number of methanol molecules that exchange their protons each time a COOH proton is transferred to a methanol molecule. Hence the kinetic order with respect to methanol is found as follows:

For the kinetic term proportional to [HBz]

$$k_1/k_1' = 1.31/0.71 = 1.85$$

For the kinetic term proportional to [HBz][NaBz]

$$k_2/k_2' = 1.21/1.52 = 0.80$$

Within experimental error, the second ratio could be 1, which is its lowest possible value. The first ratio of 1.85 is not necessarily a whole number, as it could be the average of several processes.

Data at −81.6°.— In order to determine whether the kinetic order with respect to methanol changes appreciably with the temperature, we decided to make a drastic change and made an extensive series of measurements at −81.6°. The kinetic analysis of the rates based on the CH₃ proton resonance is simpler at −81.6° than at 24.8° because the proton exchange between methyloxonium ion or methoxide ion and the solvent is negligible under our experimental conditions. Our experiments again consisted of several series, each at constant buffer ratio. For any given buffer ratio our data can be fitted to an equation involving a linear term and a quadratic term, as shown in eq. 18 and illustrated in Fig. 1.

$$R_M = j_1[HBz] + k_2[HBz][NaBz] \qquad (18)$$

The coefficient, k_2, of the quadratic term is independent of the buffer ratio and is therefore a true rate constant. However, in contrast to the corresponding results at 25°, the coefficient j_1 varied with the buffer ratio. The results are summarized in Table V. Within experimental error the variation of the coefficient j_1 with the buffer ratio is given by eq. 19.

$$j_1 = k_1 + k_3([NaBz]/[HBz])^{1/2} \qquad (19)$$

Figure 2 shows a plot of this equation. Values of the rate constants, calculated by least squares, are k_1 = 216 and k_3 = 1.07 × 10^4. As shown in the last column of Table V, the fit is very good, except possibly at the lowest ratios. Since we were puzzled by the dependence on the square root of the buffer ratio, we tried to fit the
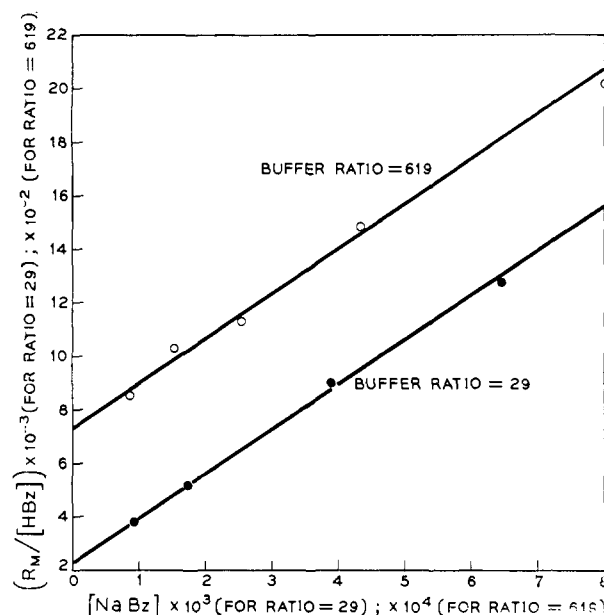

Fig. 1.—Typical kinetic plots of data at −81.6° for solutions of benzoic acid and sodium benzoate in methanol, buffer ratio = [HBz]/[NaBz].

data to a number of other rate laws, but no rate law that differed significantly from eq. 19 could fit the data at all well. For example, there was no evidence for a

TABLE V

KINETIC ANALYSIS OF R_M FOR BENZOIC ACID–SODIUM BENZOATE BUFFERS IN METHANOL AT −81.6°

$\left(\dfrac{[HBz]}{[NaBz]}\right)$	Range of 10^3 [HBz]	10$^{-6}k_2$, sec.$^{-1}$M.$^{-1}$	j_1 sec.$^{-1}$ Obsd.	Calcd.^{a}
2660	109–591	1.78	380 ± 30	423
619	47–441	1.64	750 ± 40	646
283	43–481	1.67	850 ± 50	852
98.7	22–309	1.72	1280 ± 100	1293
29.0	12–166	1.73	2210 ± 250	2203
10.5	13–270	1.91	3040 ± 400	3520
0.902	2–24	1.65	^{b}7900 ± 4000	11500

Av. 1.73 ± 0.09

^{a} Calculated from the equation j_1 = 216 + 1.07 × 10^4([NaBz]/[HBz])$^{1/2}$. ^{b} This value was not included in the least squares treatment.

kinetic term equal to k_4[NaBz], the upper limit to the magnitude of k_4 being set by our data as 2 × 10^3 sec.$^{-1}$. Thus we deduce the over-all rate law shown in eq. 20.

(20) E. Grunwald and C. F. Jumper, in preparation.

TABLE VI

EVALUATION OF RATE CONSTANTS FROM R_C FOR BENZOIC ACID–SODIUM BENZOATE BUFFER AT −81.6°

[HBz]	[Bz⁻]	R_C	Rate constant	$k_3[HBz]^{1/2}[NaBz]^{1/2}$
		1. Evaluation of k_1'		
0.342	~3 × 10⁻⁷ᵃ	30	90	—
0.813	~4 × 10⁻⁷ᵃ	90	110	—
			Av. $k_1' = 100 \pm 10$ sec.⁻¹	
		2. Evaluationᵈ of k_2'		
0.404	0.0122	7600ᵇ	1.53 × 10⁶	—
.409	.0106	9110ᶜ	2.08 × 10⁶	—
.611	.00700	7920ᵇ	1.83 × 10⁶	—
.625	.00714	8370ᶜ	1.86 × 10⁶	—
.829	.00508	8140ᵇ	1.91 × 10⁶	—
.897	.00453	6850ᶜ	1.67 × 10⁶	—
			Av. $k_2' = 1.81 \pm 0.14 \times 10^6$ sec.⁻¹ M^{-1}	
		3. Evaluationᵉ of k_3'		
0.324	5.37 × 10⁻⁵	65	200 ± 1500	45
.324ᶠ	4.10 × 10⁻⁵	65	2200 ± 1900	39
.323ᵍ	5.40 × 10⁻⁵	58	−1400 ± 1700	45
.700	27.8 × 10⁻⁵	350	−5000 ± 6000ʰ	150
			Av. $k_3' = 300 \pm 1200$ sec.⁻¹	

ᵃ No sodium benzoate was added; $pK_A = 12.7 \pm 0.5$. ᵇ Solutions were out-gassed. ᶜ Solutions were air-saturated. ᵈ $k_2' = (R_C - 100[HBz])/[HBz][NaBz]$. ᵉ $k_3' = (R_C - 100[HBz] - 1.81 \times 10^6[HBz][NaBz])/[HBz]^{1/2}[NaBz]^{1/2}$. ᶠ In the presence of 0.012 N NaCl. ᵍ In the presence of 0.0123 N (CH₃)₄NCl. ʰ Omitted from average.

$$R_M = 216[HBz] + 1.07 \times 10^4[HBz]^{1/2}[NaBz]^{1/2} + 1.73 \times 10^6[HBz][NaBz] \quad (20)$$

Values of R_C for the COOH protons were analyzed in an analogous fashion, as shown in Table VI. Values of k_1 were deduced from the width of the COOH line in solutions containing only benzoic acid. To prove that kinetic terms involving benzoate ion are negligible under these conditions, we estimated pK_A for benzoic acid from values of $R - R_M$ for the CH₃ protons and the previously reported value of $k_{MeOH_2^+}$.[11] The result for pK_A is 12.7 ± 0.5 at −81.6°, and values of [Bz⁻] based on this result are included in the table.
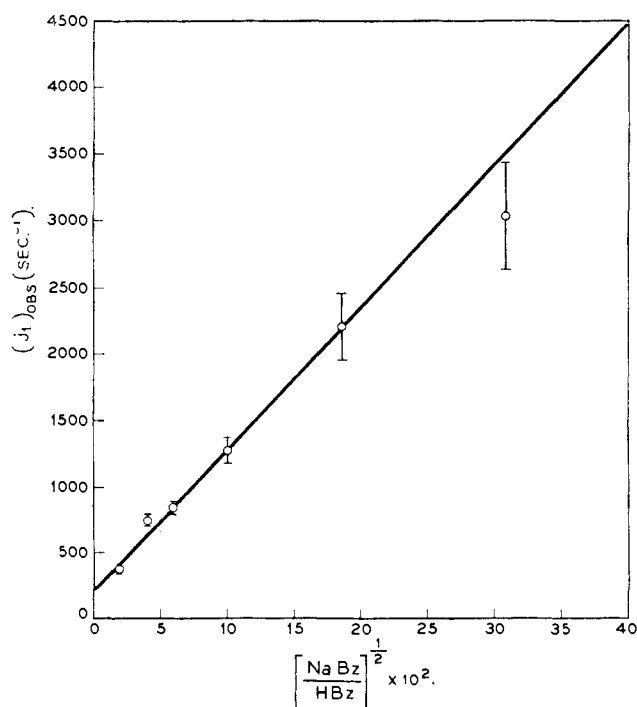

Fig. 2.—Kinetic data for solutions of benzoic acid and sodium benzoate in methanol at −81.6°, plotted according to eq. 19.

Values of k_2' were based on line width measurements of the coalesced OH–COOH line. The experiments were planned so that the term $j_1[HBz]$ was less than 10% of R_C, and $k_1'[HBz]$ was less than 2% of R_C.

Since k'_3 is much smaller than k_3, no correction was made for this kinetic term in calculating k_2'.

Measurements of k_3' from R_C were made under conditions where the term $k_3[HBz]^{1/2}[NaBz]^{1/2}$ amounted to a substantial fraction of R_M. The value of k_3' was insignificantly small, the average being 300 ± 1200 sec.⁻¹, as compared to 1.07 × 10⁴ sec.⁻¹ for k_3.

In the discussion of possible mechanisms for the observed kinetic terms, it is helpful to know whether electrolytes are largely associated in methanol at −80°. We therefore investigated briefly the conductance of KCl at −78.8°. Λ_c was found to be 7.95 ohm⁻¹ cm.² at 0.001656 N KCl, and 7.16 ohm⁻¹ cm.² at 0.01032 N KCl. The variation of Λ_c with $\sqrt{c}$ is typical of *strong* electrolytes in this concentration range, the average slope being 13.0 as compared to an Onsager limiting slope of 20.4. If ionic association were important, we would have expected the slope to be greater than the Onsager slope.[21] That salts should behave as strong electrolytes in methanol at low temperature might of course have been anticipated since the dielectric constant of methanol at −80°[22] is 56.6 and its D.T. product increases with decreasing temperature.

The rate law, eq. 20, contains the formal concentration of sodium benzoate; hence the reactant could be either the benzoate ion or the sodium ion. The sodium ion was ruled out, however, because replacement of a part of the sodium benzoate by sodium chloride resulted in a decreased rate characteristic of the decrease in the benzoate ion concentration. A control experiment using tetramethylammonium chloride instead of sodium chloride demonstrated that this was not an ionic strength effect.

The number of methanol molecules participating in each kinetic process was calculated as described before. The results are:

For the term proportional to [HBz]

$$k_1/k_1' = 216/100 = 2.16$$

For the term proportional to [HBz][NaBz]

$$k_2/k_2' = 1.73/1.81 = 0.96$$

For the term proportional to $[HBz]^{1/2}[NaBz]^{1/2}$

$$k_3/k_3' = 1.07 \times 10^4/300 = 36$$

The kinetic orders with respect to methanol for the

(21) Reference 2, Chapter 6.
(22) "International Critical Tables," Volume VI, p. 83.

k_1 and k_2 terms do not differ significantly from those found at 24.8°. The kinetic order for the k_3 term is, at best, semiquantitative. However, one may conclude with assurance that the process is polymolecular in methanol. The statistical probability is greater than 0.95 that the kinetic order with respect to methanol is at least five. On the other hand, k_3' could very well be zero, i.e., the carboxyl group does not exchange at all in this process.

Average enthalpies and entropies of activation were computed using the transition-state theory[23] and are:

For k_1', $\Delta H^{\ddagger} = 6{,}530$ cal., $\Delta S^{\ddagger} = -14.4_2$ e.u.

For k_2, $\Delta H^{\ddagger} = 4{,}060$ cal., $\Delta S^{\ddagger} = -7.9_2$ e.u.

Discussion

k_1 **Term.**—A striking feature of the k_1 term is its large magnitude. A rate of exchange proportional to the benzoic acid concentration is of course to be expected because of acid dissociation. However, we shall show that k_1 exceeds by far the upper limit to the rate constant to be exected for this process. For the dynamic equilibrium

$$HBz \underset{k_-}{\overset{k_+}{\rightleftarrows}} H^+ + Bz^- \qquad (21)$$
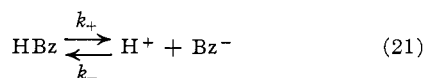
the equilibrium constant, K_A, is equal to k_+/k_-. The contribution of the acid dissociation to R_C is equal to k_+[HBz]. Since K_A is known, an upper limit of k_+ can be estimated by assuming that the reverse process takes place at each encounter. Using a formula[24] derived by Debye[25] and appropriate experimental data, we obtain 6.6×10^{10} sec.$^{-1}$ M^{-1} for the upper limit to k_-. Using the value, $K_A = 3.9 \times 10^{-10}$ for benzoic acid at 25°,[11] the upper limit to k_+ is found to be 26 sec.$^{-1}$. By contrast, k_1' is 7.1×10^4 sec.$^{-1}$, or about 2700 times greater.

We conclude therefore that practically all of the rate is due to some sort of cyclic process which does not involve dissociation to free ions.

In considering the mechanism of this cyclic process, we must bear in mind that on the average it involves approximately two methanol molecules. In fact, within experimental error, the number of methanol molecules could be exactly two, and we therefore need not exclude models requiring transition states of definite 2:1 composition. Within this framework three types of processes are possible.

(1) A concerted transfer of three protons within a cyclic solvation complex such as 22.


(22)
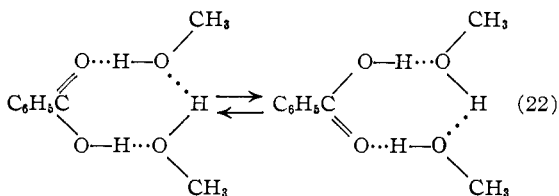
(2) Exchange accompanying the reversible ionization to an intimate ion pair. There are many possible detailed mechanisms; an example is shown in eq. 23. In this mechanism the average order with respect to methanol need not be precisely two.

(3) In the preceding mechanisms it is assumed that the methanol molecules in the solvation shell exchange rapidly with the solvent molecules, and that the proton transfer is the rate-determining step. A third mecha-


(23)
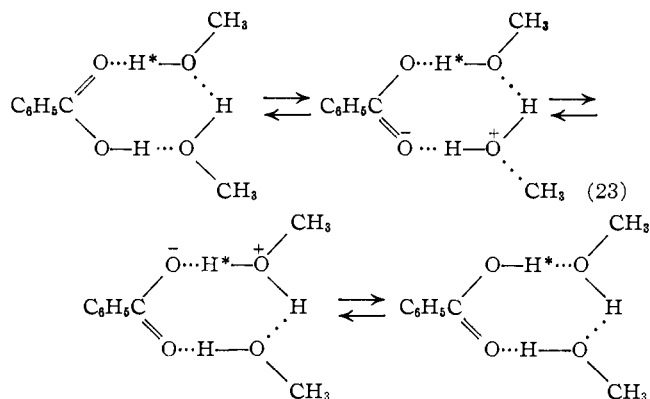
nism is obtained if we make the opposite assumption. In this case k_1 is the rate constant for the dissociation of the solvation complex.

We regard mechanism 3 as improbable because k_1 is too small. An approximate lower limit to the rate constant to be expected for the dissociation of the cyclic solvation complex can be estimated from the known rate constants for the dissociation of carboxylic acid dimers. For benzoic acid dimer this rate constant is 7.4×10^{-5} sec.$^{-1}$ in carbon tetrachloride and 3.7×10^6 sec.$^{-1}$ in toluene at 25°,[26] or an order of magnitude greater than k_1. Another reason for considering this mechanism as improbable is the rather negative entropy of activation. The observed value is plausible for a cyclic mechanism, such as 1 or 2, but not for the dissociation of a solvation complex.

On the other hand, we have at present no firm basis for choosing between mechanism 1 and mechanism 2. A study of the dependence of k_1 on acid strength which illuminates this question will be reported later.

k_2 **Term.**—This process involves one molecule of benzoic acid, one of benzoate and one of methanol. It is probable that the protons transfer by a push-pull mechanism similar to that envisaged by Swain for the ionization of alkylammonium ions in methanol.[27]

(24)
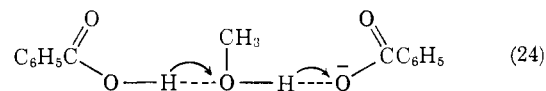
k_3 **Term.**—This term is significant only at low temperature, and our experiments show that the rate is proportional to $[HBz]^{1/2}[NaBz]^{1/2}$, at least at acid-base ratios greater than 1. We have not been able to invent a reasonable mechanism which will explain this term. In fact it is not clear whether this term represents a separate kinetic process, or whether it is due to a concentration dependence of the number of methanol molecules involved in the k_1 or k_2 processes. In the latter case k_3' would be zero, a value not ruled out by the experiments.

The k_3 term has been very intriguing to us, and a number of rather speculative mechanisms have come to mind. We feel, however, that these speculations are too uncertain to be presented without additional evidence. Further studies on other buffers are in progress and, we hope, will shed more light on this problem.

Experimental

Materials.—Solvent methanol was prepared as described previously.[11]

Benzoic acid for the experiments at −81.6° was National Bureau of Standards Calorimetric standard sample No. 39h. For the experiments at 24.8° a sample of reagent grade benzoic

(23) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14. eq. 24.

(24) M. T. Emerson, E. Grunwald and R. A. Kromhout, J. Chem. Phys., 33, 547 (1960), eq. 18.

(25) P. Debye, Trans. Am. Electrochem. Soc., 82, 265 (1942).

(26) W. Maier, L. Borucki, B. Dischler, P. Manogg and H. Rieseberg, Z. physik. Chem. (Frankfurt), 26, 27 (1960).

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

acid which had been three times recrystallized from water was used.

Sodium methoxide was prepared from reagent grade sodium and pure methanol. The sodium pellets were first freed of surface impurities by one washing with ether and several washings with pure methanol. The final solution was standardized by potentiometric titration, using constant boiling hydrochloric acid as primary acidimetric standard.[28]

Preparation of Solutions.—The buffered solutions were prepared from fresh solutions of benzoic acid and sodium methoxide in methanol. The synthetic titers were confirmed by potentiometric titration in anhydrous methanol. Satisfactory end-points could be obtained in the titration of sodium benzoate with hydrochloric acid even in solutions of concentration as low as 2×10^{-4} M and acid/base ratios as high as 2700. At the latter acid/base ratio the benzoate concentration, as calculated from the amounts of benzoic acid and sodium methoxide used in the solution preparation, was 6% less than the analytical value. This gives an estimate of 0.002 mole per cent for the benzoate impurity in the sample of benzoic acid obtained from the National Bureau of Standards. In a few cases, a very high acid/base ratio was checked by measuring the pH of the solutions with glass and calomel electrodes. The pH meter was calibrated in methanol with a benzoic acid–sodium benzoate solution of known, somewhat higher, pH.

All of the reaction mixtures were analyzed for water by Karl Fischer titration after the completion of the experiment. The water titers were usually below 0.01 molar, and always below 0.02 molar. The kinetic effect of water in buffered solutions is quite small; the deliberate addition of 1 M water to one of the solutions caused a doubling of R_M.

In experiments involving acid/base ratios greater than 1000 the glassware was pretreated with solutions of the same nominal concentration, as described in a previous paper.[11]

Most of our experiments were done in air-saturated solutions. However, we did a few experiments in outgassed samples. Outgassing did not significantly affect the coefficient m in eq. 9 and 10, nor did it have a significant effect on the rate, as illustrated in Table VI.

The air-saturated samples were sealed with corks lined with Saran, and were further sealed against the possible seepage of atmospheric moisture by a strip of Parafilm (paraffin-coated polyethylene). The procedure gave satisfactory seals, and eliminated the danger of changes of composition which is always present when sample tubes are sealed with a torch.

Instrumental.—All measurements were made at a frequency of 60 Mc. per second. Details concerning the instrument and measuring techniques have been reported in a previous paper.[11] Great care was always exercised in obtaining the highest possible homogeneity and stability. Measurements were rejected if $(1/T_2)_{ref}$ changed by more than 20% during a measurement.

Temperature control was within $\pm 0.25°$ at $-81.6°$ and within $\pm 0.05°$ at 24.8°.

Conductance Measurements.—The conductance of KCl in methanol was measured by standard techniques at $-78.8°$ to a precision of $\pm 0.25\%$. Temperature control was obtained by immersing the cell in a Dry Ice–acetone bath. The cell constant was determined at 25° with KCl in methanol.[29]

(28) C. W. Foulk and M. Hollingsworth, J. Am. Chem. Soc., **45**, 1220 (1923).

(29) J. P. Butler, H. I. Schiff and A. P. Gordon, J. Chem. Phys., **19**, 752 (1951).

Decay Kinetics of the 1-Naphthaldehyde and Benzophenone Triplet States in Benzene[1a]

BY JERRY A. BELL AND HENRY LINSCHITZ

Flash excitation studies have been made on the metastable (triplet) states of 1-naphthaldehyde and benzophenone in benzene solution with added hydrogen donors and heavy metal chelates. This technique permits direct measurement of the rate constants for triplet decay, k_d, hydrogen abstraction, k_r, and triplet quenching, k_q. The ratios k_d/k_r and k_q/k_r calculated from the direct measurements agree well with previous values for the ratios obtained from photochemical data. The effect of impurities is discussed and found to play a major role in the decay of triplet states in solution. The short lifetime of benzophenone triplet in benzene solution seems to be anomalous.

The excited state involved in the photochemical formation of pinacols from aromatic carbonyl compounds has been identified as the lowest triplet state of the carbonyl.[1b–3] Recent work on this reaction has been directed toward the measurement of the relevant rate constants for processes involving the excited state, such as energy degradation or hydrogen abstraction.[2] The ratios of these rate constants are readily obtained by standard photochemical kinetic methods, but the absolute values are, of course, more difficult to establish. In the case of the reaction between benzophenone and various donors, Hammond, et al.,[2] have measured the effect of various quenching species on the quantum yield of benzophenone disappearance. Making the assumption that the quenching process is diffusion controlled, the quenching rate constant was estimated and the other kinetic constants evaluated. For benzophenone, absolute lifetimes were obtained which were in good agreement with those deduced by Bäckstrom and Sandros[3] from a study of the benzophenone sensitized phosphorescence of biacetyl. Here again, how-

ever, it was necessary to assume a diffusion controlled rate for the energy transfer process.

Previous attempts to observe directly the triplet state of benzophenone in photochemically active fluid solvents were unsuccessful, due essentially to the short lifetime of the triplet and the overlap of its absorption with that of the ketyl radical.[4,5] Using flash excitation equipment with short time resolution, we have now been able to distinguish the short-lived triplet from the ketyl radical and to measure directly the rate constants for hydrogen abstraction and energy degradation.

1-Naphthaldehyde was found not to form pinacols when irradiated in alcohols or benzene.[6] This lack of reactivity readily permits the study of energy degradation and quenching processes of the naphthaldehyde triplet by flash techniques. The naphthaldehyde triplet decay and quenching data, besides being of intrinsic interest, may be germane to the benzophenone case as can be judged by the over-all consistency of the results.

Experimental

Materials.—1-Naphthaldehyde was E. K. White Label which was twice vacuum distilled with the middle third being taken each time. The product boiled at 101° at about 1 mm. The infrared spectrum of the purified naphthaldehyde was identical

(1) (a) This work was supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (No. AT(30-1-)-2003). (b) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. Am. Chem. Soc., **80**, 1068 (1959); J. N. Pitts, H. W. Johnson and T. Kuwana, Symposium on Reversible Photochemical Processes, Durham, No. Carolina, April, 1962.

(2) (a) W. M. Moore, G. S. Hammond and R. P. Foss, J. Am. Chem. Soc., **83**, 2789 (1961); (b) C. S. Hammond, W. P. Baker and W. M. Moore, ibid., **83**, 2795 (1961).

(3) H. L. J. Bäckstrom and K. Sandros, Acta. Chem. Scand., **14**, 48 (1960).

(4) G. Porter and F. Wilkinson, Trans. Faraday Soc., **57**, 1686 (1961).

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(6) G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., **84**, 207 (1962).