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Kinetics and Mechanism of the Proton Transfer between Methyloxonium Ion and Benzoic Acid in Methanol Solution

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This paper reports n.m.r. measurements of the rate of proton transfer between methanol and benzoic acid in the presence of HCl at 24.8° and at -81.6°. Two kinetic processes are recognized: a direct exchange between benzoic acid and methanol, and a parallel process involving catalysis by methyloxonium ion. The former process is kinetically identical with one of the processes taking place in benzoic acid-benzoate buffers in methanol, and the new rate constants are in good agreement with values reported for the process previously.¹ Rate constants for the latter process are $2.58 \times 10^8 \text{ sec.}^{-1} M^{-1}$ at 24.8° and $7.5 \times 10^6 \text{ sec.}^{-1} M^{-1}$ at -81.6°; average values of ΔH^\ddagger and ΔS^\ddagger are 3.3 kcal. and -9 e.u. It is shown that the rate is too high to be accounted for by the reversible proton transfer reaction, $C_6H_5COOH + CH_3OH_2^+ = C_6H_5C(OH)_2^+ + CH_3OH$. A concerted termolecular mechanism involving one molecule each of $CH_3OH_2^+$, C_6H_5COOH and CH_3OH is proposed.

In the preceding paper¹ we reported a detailed kinetic study of the proton transfer between the carboxyl group and methanol in buffered solutions of benzoic acid. We now wish to report a supplementary study of proton transfer between methanol and benzoic acid in the presence of hydrochloric acid, which extends this work to a much lower pH range. Although the study is brief, it suffices to identify the kinetic processes. In addition to the anticipated proton exchange between benzoic acid and methanol,¹ we found a surprisingly fast reaction which involves both benzoic acid and methyloxonium ion.

Rate Measurement and Calculation

Measurements of R_C , the rate of exchange of carboxyl protons with hydroxyl protons of methanol, were made from nuclear magnetic resonance (n.m.r.) line-width determinations. Under the present conditions of low pH the methyloxonium ion-catalyzed proton exchange is so rapid that the spin-spin splitting of the HO- and CH_3^- groups in the methanol is almost completely averaged out. The spectra can therefore be interpreted in terms of an exchange between the COOH-line of benzoic acid and a single, collapsed line of the OH-protons of methanol. In only a few cases was a small correction necessary for excess width of the OH-line due to incompletely averaged out spin-spin structure. This correction can be calculated from the known rate constants for the methyloxonium ion-catalyzed exchange²; or, alternatively, the correction can be obtained experimentally since it is equal to three times the excess width of the CH_3^- resonance of methanol,¹ the latter being a quantity which is directly measurable.

At 24.8° all values of R_C were deduced from the width of the coalesced OH-COOH n.m.r. line, as described previously.¹ At -81.6° the faster rates were measured by the same method, and the slower ones were deduced from the lifetime broadening (uncertainty broadening) of the n.m.r. of the OH-protons. In the latter case, rates were computed from eq. 1

$$1/T_2' - 1/T_2 = R_C/[MeOH] \quad (1)$$

where $1/T_2$ was determined according to eq. 10 of reference 1.

Results

Experimental values of R_C at a series of benzoic acid and hydrochloric acid concentrations are summarized in Table I. Within experimental errors these results are represented by the rate laws

$$\text{At } 24.8^\circ \quad R_C = 0.71 \times 10^8 [\text{HBz}] + 2.52 \times 10^8 [\text{HBz}][\text{HCl}] \quad (2)$$

$$\text{At } -81.6^\circ \quad R_C = 126 [\text{HBz}] + 5.13 \times 10^6 [\text{HBz}][\text{HCl}] \quad (3)$$

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

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

The rate constants for the uncatalyzed exchange between benzoic acid and methanol are in good agreement with the values of k'_1 reported previously.¹

TABLE I

KINETIC RESULTS FOR SOLUTIONS OF HYDROCHLORIC AND BENZOIC ACIDS IN METHANOL

$10^5 \times [\text{HCl}]$	$[\text{HBz}]$	$(R_C/[\text{HBz}])_{\text{obsd}}$	$(R_C/[\text{HBz}])_{\text{calcd.}}^a$
Temperature -81.6°			
0.30	1.026	147	141
0.46	0.667	148	150
3.05	1.016	276	282
9.1	0.683	606	593
9.9	.995	584	633
11.6	.672	943 ^b	721
316	.676	17600	16300
Temperature 24.8°			
165	0.218	4.92×10^5	4.87×10^5
83	.222	2.42×10^5	2.80×10^5
58	.224	1.89×10^5	2.17×10^5
34	.225	1.37×10^5	1.57×10^5
8	.227	0.87×10^5	0.91×10^5
165	.440	5.12×10^5	4.87×10^5
116	.445	3.91×10^5	3.63×10^5
83	.449	2.87×10^5	2.80×10^5
57	.451	2.31×10^5	2.15×10^5
31	.454	1.71×10^5	1.49×10^5
8	.456	1.04×10^5	0.91×10^5

^a Calculated from eq. 2 and 3, respectively. ^b This value was not included in the least squares analysis.

In the HCl-catalyzed exchange between benzoic acid and methanol, the effective catalyst is the methyloxonium ion rather than the chloride ion, since it has been shown previously¹ that sodium chloride and tetramethylammonium chloride are not catalytic. For this reason the accuracy of the rate constants can be improved slightly if a small correction is made for the effect of the trace of water (*ca.* 0.005 *M*) in our solvent, since water converts methyloxonium ion to the much less reactive hydronium ion. Using for K_A of H_3O^+ in methanol the value 0.23 at 25°^{3,4} and 0.011 at -81.6°,² and assuming that H_3O^+ is completely unreactive, we obtain the corrected rate constants, $2.58 \times 10^8 M^{-1} \text{ sec.}^{-1}$ at 24.8° and $7.5 \times 10^6 M^{-1} \text{ sec.}^{-1}$ at -81.6°. The corresponding average quantities of activation are: $\Delta H^\ddagger = 3.30 \text{ kcal.}$, $\Delta S^\ddagger = -9.0 \text{ e.u.}$

Unfortunately it is not possible, because of technical difficulties, to measure the kinetic order with respect to methanol for the reaction involving methyloxonium ion and benzoic acid. Chemical difficulties prevent us from using HCl concentrations much below $10^{-5} M$. Yet at concentrations above this limit, the spin-spin splitting

(3) H. Goldschmidt and P. Dähli, *Z. physik. Chem.*, **108**, 121 (1924).

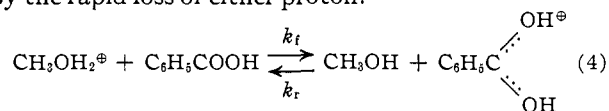
(4) L. S. Guss and I. M. Kolthoff, *J. Am. Chem. Soc.*, **62**, 1494 (1940).

of the CH_3^- and OH^- protons, upon which the measurement depends, is already almost completely averaged out because of the rapid direct exchange between methanol and methyloxonium ion.

Discussion

The first-order rate constant in eq. 2 and 3 is identical with k'_1 as defined and discussed in the preceding paper.¹

The second-order rate constant in eq. 2 and 3 refers to an exchange process involving methyloxonium ion, benzoic acid and an unknown number of methanol molecules. A possible mechanism involves the rate-determining addition of a proton to benzoic acid to give a symmetrical "onium" ion, as shown in eq. 4, followed by the rapid loss of either proton.



According to this mechanism the experimental second-order rate constant, $k_{2,\text{exp}}$, is equal to $1/2k_f$. The following estimate of k_f will show, however, that this process is much slower than the experimentally observed rate.

The estimate of k_f is made by means of the equation $k_f = k_r/K_A$, where K_A is the acid dissociation constant of $\text{C}_6\text{H}_5\text{C}(\text{OH})_2^+$ in methanol. The value of pK_A for $\text{C}_6\text{H}_5\text{C}(\text{OH})_2^+$ in water at 25° is -7.3.⁵ The change in this value upon changing the solvent from water to methanol is estimated from data⁶ for $\text{C}_6\text{H}_5\text{NH}_3^+$ and $\text{C}_6\text{H}_5\text{NH}_2\text{CH}_3^+$ as +0.8 unit. Thus pK_A is estimated as -6.5 ± 1.0 in methanol at 25°.

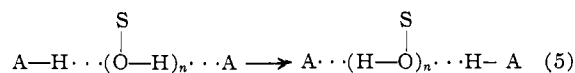
To obtain k_r , we note that $\text{C}_6\text{H}_5\text{C}(\text{OH})_2^+$ is a stronger acid than CH_3OH_2^+ . Since the rate of proton transfer from methyloxonium ion to methanol is already diffusion controlled (the most probable model involves structural diffusion^{2,7}), the rate of proton transfer from $\text{C}_6\text{H}_5\text{C}(\text{OH})_2^+$ to methanol is not likely to be much larger, and we shall assume that the two rate constants are equal. On this basis k_r is $2 \times 10^{11} \text{ sec.}^{-1}$.² Hence $1/2k_f$ is about $2 \times 10^{11}/2 \times 3 \times 10^6$, or $3 \times 10^4 M^{-1} \text{ sec.}^{-1}$. By contrast, $k_{2,\text{exp}}$ is $2.6 \times 10^8 M^{-1} \text{ sec.}^{-1}$ at 25°. Evidently the mechanism shown in eq. 4 cannot account for more than a small fraction of the observed rate.

On the other hand, pseudo-second-order rate constants in the range 10^8 – $10^9 M^{-1} \text{ sec.}^{-1}$ at room temperature are often observed for symmetrical exchange processes of the type shown in eq. 5, where SOH is a hydroxylic molecule and n is probably, but not necessarily, unity.

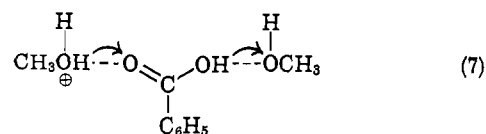
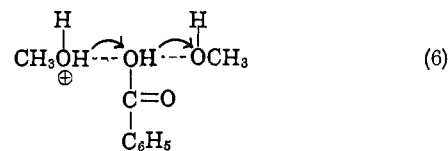
(5) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).

(6) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(7) M. Eigen and L. de Maeyer, in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, Chapter 5, and references cited therein.



Thus rate constants falling in this range have been measured at or near 25° for the systems: SOH = water, HA = NH_4^+ ,⁸ CH_3NH_3^+ ,⁹ $(\text{CH}_3)_2\text{HN}_2^+$,¹⁰ and $(\text{CH}_3)_3\text{NH}^+$ ¹⁰; SOH = methanol, HA = $\text{C}_6\text{H}_5\text{COOH}$,¹ *o*-, *m*-, and *p*-nitrobenzoic acids¹¹ and 3,5-dinitrobenzoic acid.¹¹ We therefore propose that the process taking place is either that shown in eq. 6 or that shown in eq. 7.



Not only is the observed rate constant reasonable for such a process, but also the entropy of activation is very similar to that observed in the formally analogous reaction between benzoic acid, methanol and benzoate ion.¹

Termolecular processes of the type shown in eq. 6 and 7 probably involve concerted push-pull mechanisms as envisioned by Swain.¹² In proton transfer such processes are in principle very common, the only formal requirements being that one of the molecules must be a proton donor, the other a proton acceptor, and the third both a donor and an acceptor. However, in order for the process to take place rapidly, it seems also to be necessary for the molecules to be good hydrogen-bond donors and/or acceptors. Thus the rate of a possible termolecular process involving $(\text{CH}_3)_3\text{PH}^+$, H_2O and $(\text{CH}_3)_3\text{P}$ is abnormally slow.¹³

Experimental

Chemical and n.m.r. techniques were substantially the same as described previously.^{1,2} Solutions of hydrogen chloride in methanol were prepared from pure methanol and from pure, dry hydrogen chloride which was generated in all-glass apparatus.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions with Dr. S. Meiboom.

(8) S. Meiboom, A. Loewenstein and S. Alexander, *J. Chem. Phys.*, **29**, 969 (1958).

(9) E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 630 (1957).

(10) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).

(11) E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 2047 (1963).

(12) C. G. Swain, *ibid.*, **70**, 1119 (1948); C. G. Swain and M. M. Labes, *ibid.*, **79**, 1084 (1957); C. G. Swain, J. T. McKnight and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

(13) B. Silver and Z. Luz, *ibid.*, **83**, 786 (1961).