nmr tube. As in the previous case, the uncertainty in the rate constants obtained is estimated to be on the order of 10%.

Registry No.—Isobutyraldehyde, 78-84-2; dimethylamine, 124-40-3; isobutyraldehyde-2-*d*, 4303-51-9; morpholine, 110-91-8; piperazine, 110-85-0; piperidine, 110-89-4; Me_3N, 75-50-3; $MeNH_2$, 74-89-5; N-methylpiperidine, 626-67-5; N-methylmorpholine, 109-02-4.

Acknowledgments.—We wish to acknowledge our indebtedness to the National Science Foundation for grants that permitted the purchase of the nmr spectrometer and aided in the purchase of the ultraviolet spectrophotometer, whose purchase was also made possible by a generous grant from the Charles F. Kettering Foundation.

Catalysis of α-Hydrogen Exchange. VI. Isobutyraldehyde-2-*d* Exchange in the Presence of Methylammonium Ions and Various Buffers[1]

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The kinetics of the catalysis of the dedeuteration of isobutyraldehyde-2-*d* by methylammonium chloride were studied in the presence of pyridine, 3,4-lutidine, and N-methylmorpholine buffers. Combination of the resultant data with earlier observations shows that a Brønsted plot for the dedeuteration of the iminium ion $Me_2CDCH{=}NHMe^+$ by various bases does not give a straight line. The deviations from linearity, some of which are attributed to steric hindrance, are quite similar to those observed in the Brønsted plot for the direct dedeuteration of isobutyraldehyde-2-*d* by attack of the same bases. In fact, a log–log plot of the rate constants for attack on the aldehyde *vs.* rate constants for attack on the iminium ion gives a close approach to a straight line. This observation supports the assumption that the rate-controlling step in the methylammonium ion catalyzed reaction is attack on the intermediate iminium ion. As expected, the iminium ion is less selective than the aldehyde in donating deuterium to bases.

The rate of loss of deuterium from isobutyraldehyde-2-*d* was studied in the presence of methylamine–methylammonium ion buffers, where the aldehyde exists largely in the form of its N-methylimine.[3] The major term in the kinetic equation was found to be of the form $k[Me_2CDCH{=}NMe][MeNH_3^+]$ or equivalently, $k'[Me_2CDCH{=}NHMe^+][MeNH_2]$, and the dedeuteration corresponding to this term was attributed to rate-controlling attack of methylamine on the iminium ion. The reaction rate was also studied in the presence of acetate buffers and 2,6-lutidine buffers, where the hydrogen ion concentration is much higher than in the case of methylamine buffers and the amount of aldehyde present as imine or iminium ion is too small to detect directly.[4] Under these conditions the observed reaction rate agreed with a kinetic equation containing several terms of the form $k[Me_2CDCHO][MeNH_3^+][\text{base}]$. These terms were attributed to rate-controlling attack of the various bases on N-methyliminium ions present in small concentrations in equilibrium with aldehyde and methylammonium ions, as shown in the following reaction mechanism. When the hindered base 2,6-lutidine and the relatively weakly basic acetate ions are used as buffer components the buffer base does not completely dominate the reaction.[4] It was therefore possible to learn something about the reactivity toward iminium ions of the much less abundant bases methylamine and hydroxide ions and the very weak base, water. Where reactivities were determined in two different ways, somewhat different results were obtained. These differences were attributed largely to specific medium effects on rate and equilibrium constants; such effects were found to be rather large in the presence of 2,6-lutidine buffers. The necessity of allowing for specific medium effects somewhat weakens the argument that kinetic terms of the form $k[Me_2CDCHO][MeNH_3^+][\text{base}]$ or $k'[Me_2CDCH{=}NHMe^+][\text{base}]$ are due to the same reaction mechanism with the same rate-controlling step under all the conditions that we have studied. To obtain further evidence on this point, we have now investigated the dedeuteration of isobutyraldehyde-2-*d* in the presence of methylammonium ions and several additional buffers in order to compare the relative reactivity of various bases toward isobutyraldehyde and its N-methyliminium ion.

$$\mathrm{Me_2CDCHO + B \xrightarrow{k_B} BD + Me_2C{=}CHO^-}$$
$$\mathrm{Me_2CDCHO + MeNH_3^+ \rightleftharpoons Me_2CDCH{=}NHMe^+} \quad (1)$$
$$\mathrm{Me_2CDCH{=}NHMe^+ + B \xrightarrow{k_B} BD + Me_2C{=}CHNHMe}$$

Results

If the loss of deuterium from isobutyraldehyde-2-*d* occurs by a process like that outlined (up to the rate-controlling steps) in mechanism 1, then the rate of reaction should follow eq 2, which is analogous to the kinetic equations used previously.[3,4] In this equation

$$-\mathrm{d[AD]}/\mathrm{d}t = \mathrm{[AD]}\sum_i k_{\mathrm{B}_i}[\mathrm{B}_i] + [\mathrm{HImD^+}]\sum_i k_{\mathrm{B}_i}'[\mathrm{B}_i] \quad (2)$$

AD is the deuterated aldehyde (free and hydrated), $HImD^+$ is $Me_2CDCH{=}NHMe^+$, k_{B_i} is the rate constant for the attack of the *i*th base (B_i) on isobutyr-

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[1] (a) This investigation was supported in part by Public Health Service Research Grants AM 06829 MCB and AM 10378 from the National Institute of Arthritis and Metabolic Diseases. (b) Abstracted in part from the Ph.D. thesis of J. G. Houston, Georgia Institute of Technology, 1964. (c) For the preceding paper in this series, see J. Hine and J. Mulders, *J. Org. Chem.*, **32**, 2200 (1967).

[2] (a) Author to whom inquiries should be addressed at The Ohio State University. (b) National Defense Education Act Fellow, 1960–1963.

[3] J. Hine, B. C. Menon, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **88**, 3367 (1966).

[4] J. Hine, F. C. Kokesh, K. G. Hampton, and J. Mulders, *ibid.*, **89**, 1205 (1967).

aldehyde-2-*d*, and k_{B_i}' is the rate constant for attack of B_i on the N-methyliminium ion. From values and upper limits on values for the appropriate k_{B_i} values and certain functions of k_{B_i}' values,[3-5] it is clear that catalysis by N-isobutylidenemethylamine and isobutyrate ions (from isobutyric acid present as an impurity in the aldehyde used), both of which are present in very small concentrations and are relatively ineffective catalysts, may be neglected. In order to assess the importance of catalysis by methylamine and hydroxide ions, it is necessary to use the ion product constant of water and the acidity constants of our buffer acids under the various conditions used. There seemed to be no practical way of obtaining the ion product constant of water; so we assumed that it varied with the ionic strength of the solutions used in the same way that it does in the presence of sodium chloride,[6] and that electrically neutral species have no effect on it. From a number of p*K* measurements in the presence of various concentrations of the relevant species we concluded that the p*K* of the pyridinium ion would be 5.25 ± 0.10 and the p*K* of the N-methylmorpholinium ion would be 7.45 ± 0.10 under all the conditions under which kinetic runs were made. A wider variation was found for the 3,4-lutidinium ion, but all the values obtained could be fitted by eq 3, with an average deviation of 0.005 (eq 3). Not all the possible combinations of ranges of concentrations of the various reagents were studied in the p*K* measurements made, but the resulting uncertainties are believed to be much smaller than those necessarily present in the ion product constant of water.

$$\mathrm{p}K = 6.331 - 0.452([34\mathrm{L}] + [34\mathrm{LHCl}]) + 0.055[\mathrm{MeNH_3Cl}] \quad (3)$$

Inasmuch as the concentrations of the various catalysts present remain constant throughout a given run, the rate of reaction in any given run follows a first-order rate equation where k_p is the pseudo-first-order rate constant (eq 4). Combination of eq 2 and 4 and

$$-\mathrm{d}[\mathrm{AD}]/\mathrm{d}t = k_p[\mathrm{AD}] \quad (4)$$

appropriate substitutions[3,4] give the equation

$$k_p = k_B[\mathrm{B}] + k_h[\mathrm{OH^-}] + k_w[\mathrm{H_2O}] + \left(C_1 + \frac{C_2 r}{K_{BH}} + \frac{C_3 r[\mathrm{MeNH_3^+}]}{K_{BH}} + C_4[\mathrm{B}]\right)[\mathrm{MeNH_3^+}] \quad (5)$$

where B is the basic component of the buffer, K_{BH} is the acidity constant of the acid component of the buffer, *r* is the buffer ratio ([B]/[BH$^+$]), K_{MH} is the acidity constant of methylammonium ions, k_m and k_m' are the rate constants for attack of methylamine on isobutyraldehyde-2-*d* and its N-methyliminium ion, K_w is the ion product constant of water, and

$$C_1 = \frac{KK_{MH}k_w'[\mathrm{H_2O}]}{K_{IH}}$$

$$C_2 = \left(k_m + \frac{k_h'KK_w}{K_{IH}}\right)K_{MH}$$

$$C_3 = \frac{k_m'KK_{MH}^2}{K_{IH}}$$

$$C_4 = \frac{k_B'KK_{MH}}{K_{IH}}$$

$$K_{IH} = \frac{[\mathrm{H^+}][\mathrm{Me_2CDCH{=}NMe}]}{[\mathrm{Me_2CDCH{=}NHMe^+}]}$$

$$K = \frac{[\mathrm{Me_2CDCH{=}NMe}]}{[\mathrm{AD}][\mathrm{MeNH_2}]}$$

Equation 5 may be rearranged to give

$$C_4[\mathrm{B}][\mathrm{MeNH_3^+}] = k_p - k_B[\mathrm{B}] - k_h[\mathrm{OH^-}] - k_w[\mathrm{H_2O}] - \left(C_1 + \frac{C_2 r}{K_{BH}} + \frac{C_3 r[\mathrm{MeNH_3^+}]}{K_{BH}}\right)[\mathrm{MeNH_3^+}] \quad (6)$$

The first-order rate constants obtained in the presence of methylammonium chloride and pyridine–pyridinium chloride, 3,4-lutidine-3,4-lutidinium chloride, and N-methylmorpholine-N-methylmorpholinium perchlorate buffers are listed in Tables I, II, and III, respectively. Equation 6 was used to calculate values of C_4[B][MeNH$_3^+$], which may be regarded as equal to k_p minus several "correction" terms. In all cases the k_B[B] term was at least three times as large as all the other correction terms combined. The values of C_1, C_2, and C_3 used in the calculations were those determined in experiments using 2,6-lutidine buffers.[4] The difference in the corrections calculated in this way and corrections calculated using the C_1, C_2, and C_3

TABLE I

DEUTERIUM EXCHANGE OF ISOBUTYRALDEHYDE-2-*d* IN THE PRESENCE OF METHYLAMMONIUM CHLORIDE AND PYRIDINE–PYRIDINIUM CHLORIDE BUFFERS AT 35° [a]

[MeNH$_3^+$], *M*	[Py], *M*	[PyH$^+$], *M*	10^6k_p, sec^{-1}	10^6C_4[B]-[MeNH$_3^+$], sec^{-1}
0.082	0.280	0.263	7.37	5.13
0.164	0.280	0.263	11.9	9.6
0.246	0.280	0.263	16.1	13.8
0.328	0.280	0.263	20.2	17.9
0.410	0.280	0.263	22.8	20.5
0.410	0.032	0.0766	2.25	1.91
0.410	0.0676	0.336	5.15	4.53
0.410	0.094	0.123	7.78	6.95
0.410	0.127	0.316	9.52	8.43
0.410	0.156	0.170	12.4	11.1
0.410	0.196	0.292	15.7	14.1
0.410	0.218	0.216	16.1	14.3
0.410	0.384	0.226	28.8	25.7

[a] In all runs the initial isobutyraldehyde-2-*d* concentration was 0.319 *M*.

TABLE II

DEUTERIUM EXCHANGE OF ISOBUTYRALDEHYDE-2-*d* IN THE PRESENCE OF METHYLAMMONIUM CHLORIDE AND 3,4-LUTIDINE–3,4-LUTIDINIUM CHLORIDE BUFFERS AT 35° [a]

[MeNH$_3^+$], *M*	[34-L], *M*	[34-LH$^+$], *M*	10^6k_p, sec^{-1}	10^6C_4[B]-[MeNH$_3^+$], sec^{-1}
0.085	0.191	0.486	13.8	7.6
0.170	0.191	0.486	19.2	13.0
0.255	0.191	0.486	25.3	19.1
0.340	0.191	0.486	32.2	26.0
0.425	0.191	0.486	36.5	30.3
0.425	0.0495	0.221	9.9	8.2
0.425	0.097	0.310	19.2	16.0
0.425	0.110	0.499	18.5	14.9
0.425	0.144	0.401	33.7	29.0
0.425	0.400	0.468	74.7	61.7

[a] In all runs the initial isobutyraldehyde-2-*d* concentration was 0.319 *M*.

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[5] J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **87**, 5050 (1965).

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 752, 754.

TABLE III

DEUTERIUM EXCHANGE OF ISOBUTYRALDEHYDE-2-*d* IN THE PRESENCE OF METHYLAMMONIUM CHLORIDE AND N-METHYLMORPHOLINE–N-METHYLMORPHOLINIUM PERCHLORATE AT 35° [a]

$[MeNH_3^+]$, *M*	[Nmm], *M*	$[NmmH^+]$, *M*	$10^6 k_p$, sec^{-1}	$10^6 C_4[B][MeNH_3^+]$, sec^{-1}
0.044	0.211	0.212	57.8	19.0
0.088	0.211	0.212	73.1	34.2
0.132	0.211	0.212	95.5	56.4
0.176	0.211	0.212	113	74
0.220	0.211	0.212	128	88
0.220	0.211	0.182	137[b]	97
0.030	0.187	0.075	45.0[c,d]	10.5
0.070	0.187	0.075	58.8[c,d]	24.0
0.141	0.189	0.073	65.3[c,d]	29.3
0.141	0.189	0.073	67.0[d,e]	31.0
0.176	0.187	0.075	99.0[c,d]	62.9
0.220	0.084	0.073	51.5[b]	34.9
0.220	0.106	0.091	67.5[b]	46.8
0.220	0.125	0.126	75.0	51.0
0.220	0.127	0.109	81.3[b]	56.8
0.220	0.154	0.424	112[f]	83
0.220	0.167	0.168	93.3	61.6
0.220	0.169	0.145	105[b]	73

[a] Initial isobutyraldehyde-2-*d* concentration 0.14 *M* and ionic strength 0.43 *M* (by addition of sodium perchlorate if necessary) except where otherwise noted. [b] Ionic strength 0.40 *M*. [c] Ionic strength 0.25 *M*. [d] Initial isobutyraldehyde-2-*d* concentration 0.22 *M*. [e] Ionic strength 0.34 *M*. [f] Ionic strength 0.64 *M*.

values determined in the presence of acetate and methylamine buffers was 4.8% as large as k_p in one run (using a pyridine buffer) and less than 2% as large in all other runs. A change of 0.1 in the value of p*K* used for the acid component of the buffer would never change the calculated correction by as much as 2% of the value of k_p. The values of $C_4[B][MeNH_3^+]$ for pyridine and 3,4-lutidine are plotted against the product $[B][MeNH_3^+]$ in Figure 1 and an analogous plot for N-methylmorpholine is shown in Figure 2. Most of the points fall fairly near a straight line for the given base, although there are a few rather large deviations from the line for N-methylmorpholine. The slopes of these lines are the C_4 values for the three bases. These values are 1.7 × 10^{-4}, 3.7 × 10^{-4}, and 2.0 × 10^{-3} M^{-2} sec^{-1} for pyridine, 3,4-lutidine, and N-methylmorpholine, respectively.

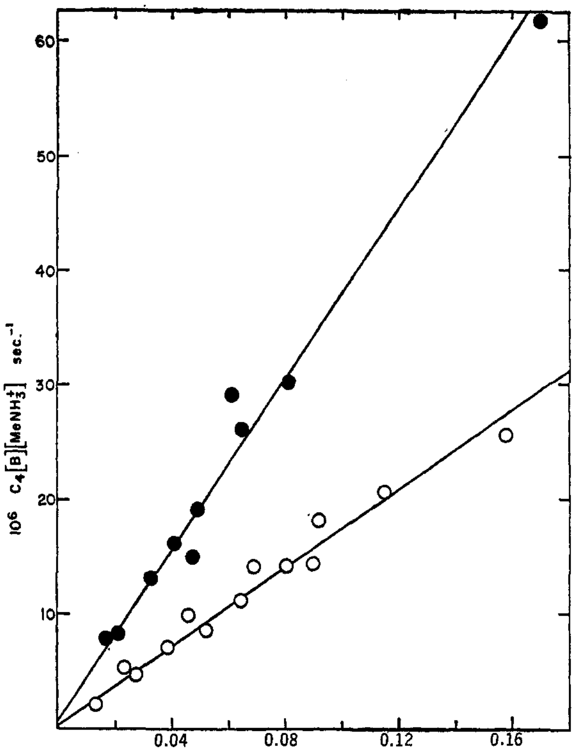


Figure 1.—Plot of $C_4[B][MeNH_3^+]$ *vs.* $[B][MeNH_3^+]$ for pyridine (open circles) and 3,4-lutidine (solid circles).

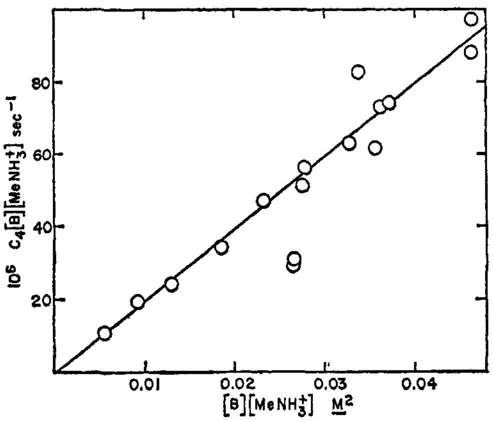


Figure 2.—Plot of $C_4[B][MeNH_3^+]$ *vs.* $[B][MeNH_3^+]$ for N-methylmorpholine.

Discussion

The C_4 values we have obtained for pyridine, 3,4-lutidine, and N-methylmorpholine are values of the function $k_B'KK_{MH}/K_{IH}$ for these bases. Although K and K_{MH} are known, the values of k_B' (the rate constants for the dedeuteration of the N-methyliminium ion of isobutyraldehyde-2-*d*) cannot be calculated because K_{IH}, the acidity constant for the N-methyliminium ion, is not known. Nevertheless, since KK_{MH}/K_{IH} should be reasonably nearly constant, comparison of the various values of $k_B'KK_{MH}/K_{IH}$ should provide a comparison of the relative abilities of the various bases to dedeuterate the iminium ion. Values are listed in Table IV for the three bases studied in the present work and for 2,6-lutidine,[4] acetate ions,[4] methylamine, water, and hydroxide ions. The appropriate value for methylamine ($k_m'KK_{MH}/K_{IH}$) is equal to C_3 divided by K_{MH}. For K_{MH} the value (3.57 × 10^{-11} *M*) at ionic strength 0.5 *M* (about that present in the relevant kinetic runs)[3,4] was used. Use of the C_3 value determined using 2,6-lutidine buffers (4.61 × 10^{-13} M^{-1} sec^{-1})[4] gives one value of $k_m'KK_{MH}/K_{IH}$ and the C_3 value determined using methylamine buffers (9.9 × 10^{-13} M^{-1} sec^{-1})[3,4] gives another. The value for water ($k_w'KK_{MH}/K_{IH}$) is equal to C_1 divided by $[H_2O]$, which was about 53 *M* in the appropriate experiments. Both the C_1 value obtained in experiments using 2,6-lutidine buffers (1.47 × 10^{-7} M^{-1} sec^{-1})[4] and the probably less reliable value obtained using acetate buffers (3.9 × 10^{-7} M^{-1} sec^{-1})[4] were used to calculate $k_w'KK_{MH}/K_{IH}$ values. The rate constant k_h' occurs only in the term C_2, which also contains the rate constant k_m. Therefore we cannot determine $k_h'KK_{MH}/K_{IH}$ unambiguously. We can determine its maximum value, however, by attributing all of C_2 to its k_h' component (*i.e.*, neglecting

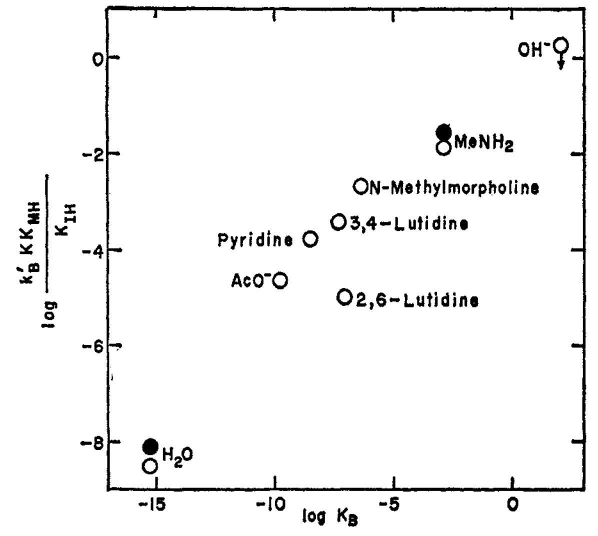


Figure 3.—Brønsted plot for the dedeuteration of $Me_2CDCH{=}NHMe^+$ by various bases. In the case of water and methylamine, the open circles refer to data obtained using 2,6-lutidine buffers and the solid circles refer to data obtained in acetate and methylamine buffers, respectively. The point with an arrow attached is a limit; the correct point may lie an unknown distance in the direction indicated.

TABLE IV

RELATIVE RATE CONSTANTS FOR DEDEUTERATION OF ISOBUTYRALDEHYDE-2-*d* AND ITS N-METHYLIMINIUM ION BY VARIOUS BASES

Base	$k_B'KK_{MH}/K_{IH}$, M^{-2} sec^{-1}	Log $k_B'KK_{MH}/K_{IH}$	Log k_B	pK_B[a]
Hydroxide ions	<1.5[b]	<0.18[b]	-1.51	-2.05[c]
Hydroxide ions	<2.4[d]	<0.38[d]		
Methylamine	1.3×10^{-2}[b]	-1.89[b]	<-2.76[b]	2.89[e,f]
Methylamine	2.8×10^{-2}[d]	-1.55[d]	<-2.57[d]	
N-Methylmorpholine	2.0×10^{-3}	-2.70	-3.74	6.39[g]
3,4-Lutidine	3.7×10^{-4}	-3.43	-4.49	7.35[g]
Pyridine	1.7×10^{-4}	-3.77	-5.10	8.54[g]
Acetate ions	2.1×10^{-5}[h]	-4.68[h]	-6.36[h]	9.74[h,i]
2,6-Lutidine	9.7×10^{-6}	-5.01	-6.55	7.07[j]
Water	2.8×10^{-9}[b]	-8.55[b]	-9.5	15.24[k]
Water	7.3×10^{-9}[l]	-8.14[l]		

[a] These are values at 35° and 0 ionic strength corrected for symmetry effects as described previously.[5] Where necessary a pK_w of 13.681 was used.[6] [b] From experiments using 2,6-lutidine buffers.[4] [c] K_B has been multiplied by a symmetry factor of 2. [d] From experiments using methylamine buffers.[3,4] [e] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (London), **A177**, 499 (1941). [f] K_B has been multiplied by a symmetry factor of 3. [g] Determined in the present investigation. [h] K_B, k_B, or $k_B'KK_{MH}/K_{IH}$ has been multiplied by a symmetry factor of $^1/_2$. [i] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 652 (1933). [j] From ref 4. [k] K_B has been multiplied by a symmetry factor of $^3/_2$. [l] From experiments using acetate buffers.[4]

k_m) and dividing by K_w, which is equal to about 4.1×10^{-14} at 35° and ionic strengths around 0.5.[6] Both the C_2 value obtained from 2,6-lutidine experiments (6.25×10^{-14} sec^{-1})[4] and the one obtained in methylamine experiments (9.7×10^{-14} sec^{-1})[3,4] were used to calculate upper limits on $k_b'KK_{MH}/K_{IH}$ listed in Table IV.

Figure 3 is a Brønsted plot for the dedeuteration of the N-methyliminium ion derived from isobutyraldehyde. The fact that log ($k_B'KK_{MH}/K_{IH}$) is plotted instead of log k_B' merely means that all the points are displaced vertically by the amount log (KK_{MH}/K_{IH}), which should be fairly nearly constant; the linearity of the plot will not be significantly affected. The two points that could have been plotted for the hydroxide ion are so close together that they have been plotted as a single point. For methylamine and water both possible points have been plotted. There are rather large deviations from linearity in the Brønsted plot. For example, although 2,6-lutidine is the most strongly basic of the three pyridine derivatives studied, it is the poorest catalyst. The same type of deviation was observed in the Brønsted plot for the dedeuteration of isobutyraldehyde-2-*d*, where it was attributed to steric hindrance.[5]

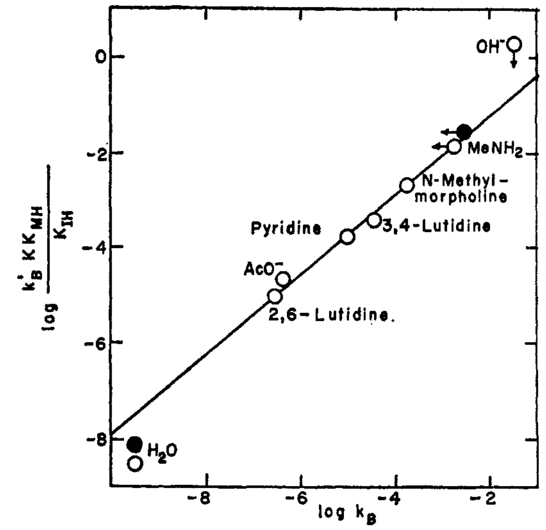
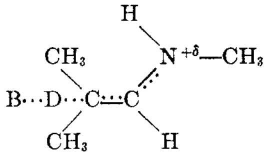


Figure 4.—Relationship between the rate constants for the dedeuteration of isobutyraldehyde-2-*d* and its N-methyliminium ion by various bases. In the case of water and methylamine the open circles refer to data obtained using 2,6-lutidine buffers and the solid circles refer to data obtained in acetate and methylamine buffers, respectively. The points with arrows attached are limits; the correct points may lie an unknown distance in the direction indicated.

In order to learn to what extent the factors that result in deviations from the Brønsted relationship for the iminium ion (Figure 3) are the same as those that result in deviations in the case of the aldehyde,[5] log ($k_B'KK_{MH}/K_{IH}$) was plotted against log k_B, as shown in Figure 4. The appropriate log k_B values[5] are listed in Table IV. The catalytic constant for methylamine (k_m) appears only in the ambiguous term C_2. By attributing all of C_2 to this term the upper limits for log k_B for methylamine listed in Table IV may be calculated using the values of C_2 determined in the presence of 2,6-lutidine buffers and of methylamine buffers. For methylamine and hydroxide ions, where the only number available for one of the two constants being plotted is an upper limit, this limit was used in the plot and an arrow is attached to the point to indicate the direction in which the actual point may lie. As in Figure 3, where two different values of C_1, C_2, and C_3 permitted the calculation of two values of k_B or $k_B'KK_{MH}/K_{IH}$, two points are plotted, except for hydroxide ions where the two points would be so close together that they are represented by a single symbol. Temporarily ignoring the points with arrows attached, it may be seen that all the points lie fairly near a straight line. In fact, the points for the five buffer bases studied lie within the experimental uncertainty of the line shown which was drawn with little consideration of the points for water. The data for water are probably subject to greater experimental uncertainty than those for any of the other five bases. When we consider this and the fact that specific solvent effects (such as those causing significant changes in the pK values for 2,6-lutidine and 3,4-lutidine at constant ionic strength) are probably causing uncertainties in the location of some of the points in Figure 4 and hence of the line drawn, we are not sure that the deviation of the points for water from the line described by the other bases is larger than the over-all experimental uncertainty. In any event, Figure 4 provides good evidence that steric factors in the attack of bases on isobutyraldehyde and its N-methyliminium ion are quite similar. If the transition state in the reaction of the iminium ion with base has the following geometry (analogous to the geometry postulated for the transition state in the reaction of the aldehyde with base[5])



in which the carbon–nitrogen framework is nearly coplanar, then only steric interference between the base and the methyl group or hydrogen atom attached to nitrogen should change the steric effects greatly at a given point along the reaction coordinate. Such interference seems highly unlikely.

The observed linearity in the plot in Figure 4, for the five buffer bases at least, strongly supports our assumption that catalysis of the deuterium exchange of isobutyraldehyde by methylammonium ions in the presence of buffer is due to the reversible formation of N-methyliminium ions which are dedeuterated by the buffer base in the rate-controlling step of the reaction. If the function of the buffer base were to catalyze some other step of the reaction, such as imine formation, it seems unlikely that steric hindrance to attack by 2,6-lutidine, for example, would be of just the proper magnitude to give the straight-line relationship observed.

The slope of the line at Figure 4 is 0.84, showing that the iminium ion is slightly less selective than the aldehyde in donating its α-deuterium to bases. Inasmuch as the α-deuterium of the iminium ion must be considerably more acidic than that of the aldehyde, the transition state would be expected to lie further along the path to products in the reactions of the aldehyde so that differences in equilibrium constants would be more fully reflected in differences in rate constants.[7,8] This difference in location of transition states does not seem to be large enough to produce a difference in steric effects, however.

The position of the line in Figure 4 helps resolve the ambiguity as to what part of the C_2 term in eq 5 is due to catalysis by attack of methylamine on the aldehyde and what part is due to attack of hydroxide ions on the N-methyliminium ion. Since the points for methylamine lie very nearly on the line and the point for hydroxide ion lies well above the line, we conclude that the k_m part is the dominant part of C_2. Using the average of the two C_2 values determined, the assumption that 9% of the C_2 term is due to its k_h' component gives a $k_h'KK_{MH}/K_{IH}$ value of 0.17 M^{-2} sec^{-1}, which moves the point for hydroxide ions down to fall on the line. This leaves 91% of the C_2 term as due to its k_m component, which corresponds to a k_m value of 1.2 or 2.5×10^{-2} M^{-2} sec^{-1}, depending on which C_3 value is used. Points for these k_m values would barely deviate perceptibly from the points (with arrows attached) for methylamine in Figure 4.

Experimental Section

Kinetic Runs.—The kinetic runs were carried out by nmr measurements of the extent of disappearance of deuterium from the isobutyraldehyde used. These measurements were carried out directly on the aqueous reaction mixtures using the techniques described previously in detail.[5]

p*K* Measurements.—The method described previously was used for the determination of pK values. Values extrapolated (from ionic strengths below 0.01 M) to infinite dilution are 5.14, 6.33, and 7.29 for pyridinium ions, 3,4-lutidinium ions, and N-methylmorpholinium ions, respectively. Essery and Schofield have reported the value 5.11 for the pyridinium ion at 35°,[9] but the acidity constants of 3,4-lutidinium and N-methylmorpholinium ions do not appear to have been reported at this temperature. From 14 to 20 pK determinations were made for each of the three buffer acids studied using concentrations of buffer salt, buffer base, and, in the case of N-methylmorpholine, sodium perchlorate, in the vicinity of those used in the various kinetic runs. In the case of the pyridinium ion all the values were between 5.19 and 5.31 and in the case of N-methylmorpholinium ions the values were between 7.44 and 7.50. The values for 3,4-lutidinium ions fit eq 3 satisfactorily.

Registry No.—Isobutyraldehyde-2-*d*, 4303-51-9; methylammonium chloride, 593-51-1; pyridine, 110-86-1; 3,4-lutidine, 583-58-4; N-methylmorpholine, 109-02-4.

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[9] J. M. Essery and K. Schofield, *J. Chem. Soc.*, 3939 (1961).