buffer solutions at 165° is approximated by the p*D* difference in these same solutions at 30°.[10] The rates of deprotonation are first order in deuterioxide ion and rates relative to the 4 position are given in Table I.

Table I. Relative Positional Rates of Hydrogen Exchange for N-Methylpyridinium Chloride (I) and Pyridine-d_5 N-Oxide (II) and of Decarboxylation of N-Methylpyridinium Carboxylates (III)

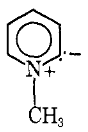
Ratio	I[a]	II[b]	III[c]
k^4/k^4	1.0	1.0	1.0
k^3/k^4	3.0	10	2.8
k^2/k^4	3400	1500	1600

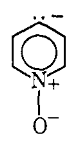
[a] In $D_2PO_4^-$–DPO_4^{2-} buffers at 165°. Position 2 has $k\psi = 7.83 \times 10^{-4}$ sec^{-1} (165°) at pD 6.46 (30°). [b] In CH_3OH–CH_3ONa at 138°. Position 2 has $k = 0.199$ M^{-1} sec^{-1}. [c] In ethylene glycol at 196.1°; data are taken from ref 6.

Hydrogen exchange was used to prepare II; each position was at least 80% deuterated. Rates of deuteration of II were obtained in CH_3OH–CH_3ONa. In basic solutions nmr signals for positions 3 and 5 overlapped with those for 4 but acidification of aliquots resulted in clean separation. Rates were first order in methoxide ion. Data for the 2,6 positions were extrapolated to 138° from results at 75 and 100°. Relative rates of exchange at 138° are given in Table I.

The kinetic data given in Table I indicate that the reactivity pattern for the deprotonation of I and II not only is qualitatively the same as that for the decarboxylation of III but also that the relative reactivities of corresponding positions within the three molecules are quantitatively similar. Reactivity is greatest adjacent to the activating heteroatom and rapidly decreases with increasing distance from this center.

The following conclusions are suggested by the results in the table. (i) Compounds I, II, and III react to form similar intermediates. Since carbanions such as IV[6] form during the decarboxylation of III, carbanionic intermediates such as IV and V are generated during hydrogen exchange. (ii) Resonance effects involving the distribution of positive charge onto carbon from nitrogen have little influence on deprotonation reactivity. Position 4 which may acquire such charge is less reactive than 3 which is not favored by such resonance. (iii) Resonance effects involving the oxygen atom of II do not seriously affect relative positional rates since the relative rate patterns for I, II, and III are similar.


IV


V

A strong likeness exists between the positional reactivity pattern found in these heteroaromatic systems and in monosubstituted carbocyclic aromatic molecules. In the latter base-catalyzed deprotonation also takes place most rapidly at an annular position adjacent to the activating substituent and decreases in the order *ortho*, *meta*, and *para*. Thus, heterocycles I and II and these carbocyclic molecules respond in fundamentally the same way in deprotonation reactions.[12]

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[10] This is a good approximation so long as the same buffer is used but, in general, is a poor one if different buffers are compared.[11]

[11] R. G. Bates, "Determination of pH. Theory and Practice," John Wiley and Sons, Inc., New York, N. Y., 1964, p 76 and Chapter 5.

[12] Pyridine constitutes a significant exception to this pattern; its positional reactivity order is reversed relative to that for I and II.[2a]

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Acid–Base Reactions and Hydrogen Exchange in Fused Acetate Eutectics. The Decomposition of Trimethylolethane

Sir:

Since many covalent organic compounds capable of hydrogen bonding with the solvent are soluble in fused salts,[1] the study of homogeneous solutions and reactions is possible as an important addition to the many known heterogeneous reactions.[2] We wish to report several interesting phenomena observed in the ternary eutectic, lithium–potassium–sodium acetate (32–30–38 mol %, mp 162°).[3]

This fused-salt solvent is quite basic. Phenolic indicators such as alizarin, alizarin yellow, *p*-nitrophenol, and *m*-nitrophenol ionize to give the colors of their conjugate bases, as alizarin does in fused K^+,Na^+–SCN^- with sodium hydroxide.[1b,4] The less acidic aromatic amine indicators differ in degree of dissociation, depending on the substituent: 2,4-dinitroaniline (pK_a = 15.00 in methanol at 20°)[5] is dissociated in 0.1% solutions in K^+,Li^+,Na^+–OAc^- at 200° while *o*-nitroaniline (pK_a = 17.88) and *p*-nitroaniline (pK_a = 18.37) are chiefly undissociated. It is more quantitatively significant to specify the extent of indicator dissociation at a known acid concentration: in 0.074 *M* acetic acid in the fused salt, the concentrations of dissociated and undissociated 2,4-dinitroaniline appear approximately equal. The equilibrium constant for the reaction, $ArNH_2 + OAc^- \rightarrow ArNH^- + HOAc$ is, therefore, about 4.5×10^{-3}, the density of the fused salt being 1.39 g/ml at 200°.

Exchange of the hydrogen atoms in the methyl groups takes place in K^+,Na^+–OAc^- eutectic (54–46 mol %, mp 233°)[6] to the extent of 40% in 10 hr at 250°. The nmr singlet of CH_3COO^- changes, in the presence of CD_3COO^-, to the triplet of CH_2DCOO^- and the quintet of CHD_2COO^- due to the geminal H–D coupling constant of 2.10 ± 0.05 cps, comparable to 2.32 ± 0.07 for CH_2DCOOH.[7] Each deuterium substitution causes an upfield chemical shift of 1.3 cps at 100 Mc.

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[1] (a) O. K. Khaishbashev, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 587 (1945); *Chem. Abstr.*, **40**, 5981[1] (1946); (b) T. I. Crowell and P. Hillery, *J. Org. Chem.*, **30**, 1339 (1965); (c) J. E. Gordon, unpublished review.

[2] W. Sundermeyer, *Angew. Chem. Int. Ed. Engl.*, **4**, 222 (1965).

[3] E. I. Pochtakova, *Zh. Neorg. Khim.*, **10**, 2333 (1965); *Russ. J. Inorg. Chem.*, **10**, 1268 (1965). We used the slightly different proportions, 32–27–41 mol %, published earlier: G. C. Diogenov, *Zh. Neorg. Khim.*, **1**, 2551 (1956); *Chem. Abstr.*, **51**, 7825*d* (1957).

[4] B. J. Brough, D. H. Kerridge, and M. Mosley, *J. Chem. Soc., A*, 1556 (1966).

[5] R. A. M. O'Ferrall and J. H. Ridd, *ibid.*, 5030 (1963).

[6] F. J. Hazlewood, E. Rhodes, and A. K. Ubbelohde, *Trans. Faraday Soc.*, **62**, 3101 (1966).

[7] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962).

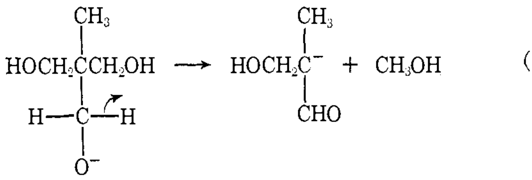
If the mechanism of the exchange were a simple proton transfer, the dianion $[CH_2{=}CO_2^{2-} \leftrightarrow {}^-CH_2\text{–}COO^-]$ would be an intermediate, but multicenter or intramolecular mechanisms are also possible.

When dissolved in the ternary eutectic at 200°, trimethylolethane ($R = CH_3$) and trimethylolpropane ($R = C_2H_5$) decompose to the same products observed when the molten triols are heated at 240–260° with alumina:[8] $RC(CH_2OH)_3 \rightarrow CH_2{=}CRCHO + CH_3OH + H_2O$.

The reaction was conducted in a vacuum system at 0.5 mm pressure, and the products were condensed in a cold trap. Trimethylolethane reacts quantitatively, with rate constant 3.5×10^{-5} sec^{-1} after a 40-min induction period. The activation energy is low, roughly 7 kcal/mol, so that $\Delta S^{\ddagger}$ is large and negative. The reaction is inhibited by acetic acid. The induction period is eliminated when sodium hydroxide, insoluble in the fused salt, is added.

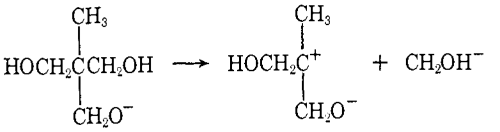
These facts are consistent with a mechanism involving appreciable accumulation of the alkoxide ion (eq 1 and 2). The enolate ion loses hydroxyl ion to form α-methylacrolein.

$$\mathrm{(CH_2OH)_2CH_3CCH_2OH + OAc^- \longrightarrow (CH_2OH)_2CH_3CCH_2O^- + HOAc} \quad (1)$$



$$\mathrm{HOCH_2\overset{CH_3}{\underset{H-\underset{O^-}{C}-H}{C}}CH_2OH \longrightarrow HOCH_2\overset{CH_3}{\underset{CHO}{C^-}} + CH_3OH} \quad (2)$$

The internal displacement by hydride ion (eq 2) is formulated in preference to loss of formaldehyde from the original alkoxide ion. The formaldehyde would have to be quantitatively reduced to methanol before vaporizing from the hot solution into the vacuum; actually, formaldehyde was reduced neither by the fused acetate nor by ethanol or trimethylolethane in the melt. A dissociation to a tertiary carbonium ion and CH_2OH^- (not a known leaving group in ordinary solvents), as in eq 3, was proposed for the alumina-catalyzed reaction.



$$\mathrm{HOCH_2\overset{CH_3}{\underset{CH_2O^-}{C}}CH_2OH \longrightarrow HOCH_2\overset{CH_3}{\underset{CH_2O^-}{C^+}} + CH_2OH^-} \quad (3)$$

Assistance by the neighboring alkoxide would yield the epoxide. However, when the reaction was run with $CH_3C(CH_2OD)_3$, no deuterium was found in the methyl group of the methanol (nor in the α-methylacrolein) as would be expected if step 3 took place.

The usefulness of molten acetate eutectics as basic, nonvolatile solvents for high-temperature organic reactions is being investigated further.

Acknowledgment. We are very grateful for the support of the U. S. Army Research Office, Durham, N. C.

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[8] R. W. Brown and G. Dougherty, *J. Org. Chem.*, **13**, 173 (1948).

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Metal Ion–Aromatic Complexes. VI. Benzene π Complexes of Metals of the Third, Fourth, and Fifth Groups

Sir:

As part of a systematic study of metal ion–aromatic complexes, we have prepared and characterized a series of unusual complexes that are of import to the nature of the aromatic–metal bond.

We have previously reported the preparation and crystal structure of Ag(I),[1] Cu(I),[2,3] and Hg(I)[4] benzene complexes. The first two are nonaxial complexes (*i.e.*, the metal ion does not lie in the sixfold symmetry axis of benzene) in agreement with theoretical predictions; however, the anion plays more than a passive role, as evidenced by the length of the M–Cl bonds. The third involves Hg_2^{2+} ions. Rundle and Corbett[5] reported the existence of a benzene complex of Ga(I) which in the absence of analytical data was presumed to be the 1:1 complex, $C_6H_6 \cdot GaGaCl_4$; further, they remarked that $GaAlCl_4$ also complexes, but $TlAlCl_4$ does not. By previously reported methods[1-3] we have prepared two benzene complexes of Tl(I): $C_6H_6 \cdot 2TlAlCl_4$ and $(C_6H_6)_2 \cdot TlAlCl_4$. These are the only known organometallic complexes of Tl(I) except for TlC_5H_5.[6] These have been characterized by, at least, duplicate chemical analysis of the inorganic components, and the benzene has been quantitatively determined by vpc after hydrolysis of the complex. *Anal.* Calcd for $C_6H_6 \cdot 2TlAlCl_4$: Tl, 49.58; Al, 6.55; Cl, 34.44; C_6H_6, 9.46. Found: Tl, 49.79; Al, 6.66; Cl, 34.48; C_6H_6, 8.31. Calcd for $(C_6H_6)_2 \cdot TlAlCl_4$: Tl, 38.62; Al, 5.10; Cl, 26.80; C_6H_6, 29.48. Found: Tl, 37.84; Al, 5.23; Cl, 25.95; C_6H_6, 28.53. Although these chemical analyses are not as accurate as we desire, we had sent samples to two commercial laboratories and they were notoriously poor, and we have performed these analyses ourselves by standard methods. Not only is care necessary to exclude oxygen and water vapor but the aromatic can be lost by prolonged exposure in a drybox. This is particularly true of $(C_6H_6)_2 \cdot TlAlCl_4$. These statements apply to the other analyses below. In general, these compounds are either insoluble in nonpolar solvents (except benzene) or the aromatic is stripped off so that further characterization in solution is not possible. $(C_6H_6)_2 \cdot TlAlCl_4$ can be readily transformed into the more stable $C_6H_6 \cdot 2(TlAlCl_4)$ under vacuum at ambient temperature. Infrared spectra of fluorocarbon mulls show no absorptions that would indicate a symmetry lower than D_{6h} for either of these complexes. This, nevertheless, is not definitive. Preliminary experiments indicate that In(I) also forms benzene complexes. We have found no evidence for a 1:1 $C_6H_6 \cdot Tl(I)$ complex.

It is interesting to note that the arguments of Rundle and Corbett based on the charge-transfer theory of Mulliken[7] can be used to predict a symmetric C_{6v} ferrocene sandwich-type structure for 2Bz·Tl(I) since

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[1] R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 3243 (1966).

[2] R. W. Turner and E. L. Amma, *ibid.*, **85**, 4046 (1963).

[3] R. W. Turner and E. L. Amma, *ibid.*, **88**, 1877 (1966).

[4] R. W. Turner and E. L. Amma, *J. Inorg. Nucl. Chem.*, **28**, 2411 (1966).

[5] R. E. Rundle and J. D. Corbett, *J. Am. Chem. Soc.*, **79**, 757 (1957).

[6] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 454.

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