lowing rearrangements: (1) 7,1–7,2 "double Wagner–Meerwein" (DWM);[5] (2) 6,1–6,2 Wagner–Meerwein (WM); (3) Nametkin (32M);[6] (4) 3,2-endo hydroxyl; (5) 6,1–6,2 Wagner–Meerwein (WM),[5] and, finally, ring opening and dehydrogenation. One process in the foregoing mechanism has never been observed, namely the 3,2-endo shift of hydroxyl,[7,8] and Rodig and Sysko expressed considerable doubt concerning its validity. Rationalizing the data[3] is difficult, in that there are several thousand possible intermediates, whose enumeration and subsequent untangling by conventional methods is a formidable task. We have therefore applied our program[2] to the rearrangement of protonated camphor (Figure 1),[3] permitting WM, DWM, 6,2-hydride (62H),[9] 32H,[7] 32M (Nametkin),[6] and 3,2-exo hydroxyl (32O) shifts. No endo migrations were allowed. The results are illustrated in Scheme I (whose scheme contributes 90% to the overall reaction) and in Scheme II (10% contribution). The mechanism offered by these two schemes is completely consistent with the isotopic data,[3] is simpler than the explanations which were previously[3,4] proposed, and requires no endo migrations. When either DWM or 32O were omitted from the program, there were no satisfactory explanations for the results. Because of the thousands of intermediates possible in the rearrangement[3] of camphor-$^{14}C_2$ in sulfuric acid, the true situation could be more complicated than indicated by Schemes I and II. For example, we certainly cannot rule out some redistribution of carbon-14 between the 7-syn and the bridgehead methyl by the mechanism[10] proposed earlier for camphor racemization. In this connection it is interesting that even with DWM and 32O, we could not improve on these earlier mechanisms for the racemization of camphor[10] and fenchone.[3]

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Basic Strength of Acetic Acid and $K^{f}_{\mathrm{IH^+}}$ Values of Some Hammett Indicators in Acetonitrile

Sir:

In an early study,[1] we employed a solution of perchloric acid in anhydrous acetic acid for the determination of $K^{f}_{\mathrm{IH^+}}$ values of three Hammett indicators in acetonitrile (AN). Reference[2,3] was made to the fact that perchloric acid was added in the form of protonated acetic acid–perchlorate ion pair $CH_3COOH_2^+ClO_4^-$. It was tacitly assumed that AN is a stronger base than acetic acid and that reaction 1 is virtually

$$CH_3COOH_2^+ClO_4^- + CH_3CN \rightleftharpoons CH_3CNH^+ (H_s^+) + ClO_4^- + CH_3COOH \quad (1)$$

instantaneous and quantitative.

Recently, Kinugasa *et al.*,[4] found that pure perchloric acid in a freshly prepared solution in AN is a relatively weak acid and that addition of acetic acid greatly increases the conductance of such a solution. Their results cast some doubt on the correctness of our values[1] of $K^{f}_{\mathrm{IH^+}}$ of 2-nitroaniline (and the two other Hammett indicators). Since the calibration of the glass electrode for pa_H measurements in AN[5] was based in part on the value of $K^{f}_{\mathrm{IH^+}}$ of 2-nitroaniline (2-NA), the previously reported value[1] has been redetermined in acetic acid free methanesulfonic acid and recalculated in perchloric acid, taking the effect of acetic acid into account. In order to do this we have determined $K^{f}_{\mathrm{CH_3COOH_2^+}}$ by measuring $[IH^+]/[I]$ of 2-nitro-4-chloroaniline (2-N-4ClA) and 2-nitro-4,5-dichloroaniline (2-N-4,5Cl_2A) in solutions of perchloric acid in AN containing various concentrations of acetic acid. Perchloric acid was added as 0.485 *M* solution in acetic acid. Extrapolation of $[IH^+]/[I]$ to zero concentration of acetic acid yielded $K^{f}_{\mathrm{IH^+}}$. In separate experiments it was found that formation of $I\cdot HOOCCH_3$ and $IH^+\cdot CH_3COOH$ is negligible. An example of the estimation of $K^{f}_{\mathrm{IH^+}}$ of 2-N-4ClA and $K^{f}_{\mathrm{CH_3COOH_2^+}}$ is given in Table I.

Table I. Determination of $K^{f}_{\mathrm{IH^+}}$ of 2-Nitro-4-chloroaniline (I) and of $K^{f}_{\mathrm{CH_3COOH_2^+}}$ in Perchloric Acid

[HAc], *M*	$[IH^+]/[I]$	$[IH^+]$, $M \times 10^4$	$[H_s^+]$,[c] $M \times 10^4$	$[CH_3COOH_2^+]$, $M \times 10^4$	$K^{f}_{\mathrm{CH_3COOH_2^+}}$[b]
0	(13.0)[a]	1.23			
0.0244	10.$_0$	1.23	3.7		
0.0694	7.$_1$	1.16	3.5	1.5	(6.4)
0.108	5.$_1$	1.12	2.6	2.6	9.3
0.198	3.$_1$	1.02	1.5	3.7	11.2
0.256	2.$_4$	0.95	1.2	4.1	13.0
0.412	1.$_7$	0.84	0.8$_3$	4.6	13.1
0.474	1.$_3$	0.75	0.6$_3$	4.9	16.0
					Av 12

[a] Extrapolation yields log $K^{f}_{\mathrm{IH^+}} = 4.3$. [b] An average value of log $K^{f}_{\mathrm{IH^+}} = 4.2$ (see Table II) was used to calculate $K^{f}_{\mathrm{CH_3COOH_2^+}}$. [c] $C_I = 1.35 \times 10^{-4}\ M$; $C_{HClO_4} = 6.26 \times 10^{-4}\ M$.

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Table II. Values of Log $K^{\mathrm{f}}_{\mathrm{IH^+}}$ of Three Hammett Indicators and of $K^{\mathrm{f}}_{\mathrm{CH_3COOH_2^+}}$

	Log $K^{\mathrm{f}}_{\mathrm{IH^+}}$			
Acid system	2-NA	2-N-4ClA	2-N-4,5Cl_2A	$K^{\mathrm{f}}_{\mathrm{CH_3COOH_2^+}}$
$HClO_4$	4.9[a] (4.85)[b]	4.2[c] (4.0)[a] (3.9)[b]	3.1[c]	12.0[c]
CH_3SO_3H	4.95[c] (4.9)[d]	4.2[c]		13.0,[e] 7[c]

[a] Reference 2, considering protonation of acetic acid. [b] Reference 2, neglecting protonation of acetic acid. [c] Present work, spectrophotometric, average value of different determinations. [d] Reference 3, spectrophotometric, in mixtures of methanesulfonic acid and its tetraethylammonium salt. [e] This work, conductometric, in solutions of the acid.

The values of $K^{\mathrm{f}}_{\mathrm{IH^+}}$ of 2-NA and 2-N-4ClA were also obtained from $[\mathrm{IH^+}]/[\mathrm{I}]$ ratios found spectrophotometrically in fresh acetic acid free solutions of methanesulfonic acid, knowing $\mathrm{p}K_{2\mathrm{HA}}$ ($K_{2\mathrm{HA}} = a_{\mathrm{H^+}}a_{\mathrm{HA_2^-}}/\{\mathrm{HA}]^2$). In this study $\mathrm{p}K_{2\mathrm{HA}}$ was redetermined conductometrically and found equal to 6.05, in agreement with that previously reported.[3] The value of $K^{\mathrm{f}}_{\mathrm{CH_3COOH_2^+}}$ was found conductometrically and also spectrophotometrically with 2-N-4ClA as indicator in methanesulfonic acid solutions containing acetic acid. In the calculation of $[\mathrm{H_s^+}]$, homoconjugation (HA_2^-) and heteroconjugation ($A^- \cdots HOOCCH_3$) were taken into account. The latter was found to be negligible under the experimental conditions. A summary of values of log $K^{\mathrm{f}}_{\mathrm{IH^+}}$ and $K^{\mathrm{f}}_{\mathrm{CH_4COOH_2^+}}$ obtained by the various methods is presented in Table II. The reason why the new value of $K^{\mathrm{f}}_{\mathrm{IH^+}}$ of 2-NA as determined in dilute perchloric acid is the same as that determined previously[1] is that the concentration of acetic acid added with the perchloric acid was so small the correction was negligible. Calculated values of $\mathrm{p}a_{\mathrm{H}}$ in 2-NA–perchloric acid mixtures used in the calibration of the glass electrode[5] are only 0.03–0.04 unit greater than previously reported at the highest acetic acid concentration encountered when the effect of the acid is taken into account.

From values of log $K^{\mathrm{f}}_{\mathrm{BH^+}}$ of acetonitrile (−10.1,[6] −10.8,[7] and ~9.5[8]) and of acetic acid (−6.2,[9] −6.1[10]) referred to water as solvent, it is clear that the basicity of acetic acid in water is stronger than that of AN. Qualitatively, the same behavior is found in AN.

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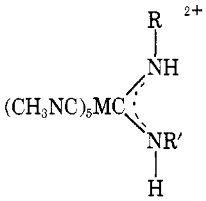
Mobility of Substituents in Metal Carbene Complexes about an FeC_6 or RuC_6 Core through Chelate Ring Formation

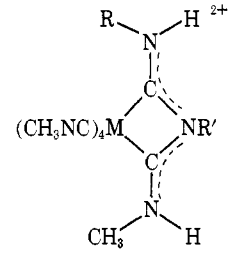
Sir:

The formation or rupture of chelate rings without breaking of a metal ligand bond is a relatively rare occurrence in transition metal chemistry, although such reactions have been frequently utilized in the construction of macrocyclic ligands.[1] Here we report on the importance of such a reaction in the chemistry of metal isocyanide complexes in which other chelate rings are not present to stabilize the metal–ligand bonds. Generally the reaction of a primary amine with an isocyanide complex results in the attack of the amine upon one isocyanide to yield a monodentate diaminocarbene ligand.[2] The results described below indicate that in certain cases the carbene and isocyanide substituents appended to the basic metal–carbon core may migrate in a reversible chelation process which can result in the conversion of the original amine nitrogen and its substituent into an isocyanide ligand.

When an amine adds to a six-coordinate isocyanide complex, either of the isomers **1** or **2** may be formed.



1



2

Steric effects appear to be dominant in determining which isomer is formed. The reaction of methylamine with hexakis(methyl isocyanide)ruthenium(II) in refluxing methanol for 15 min yields **1** (M = Ru; R = R′ = CH_3). Spectroscopic data important to the characterization of this and other complexes are set out in Table I.[3] Longer reaction times produce a ruthenium complex containing two monodentate diaminocarbene ligands. Ethylamine also reacts with hexakis(methyl isocyanide)ruthenium(II) to yield **1** (M = Ru; R = CH_3, R′ = C_2H_5; and R = C_2H_5, R′ = CH_3) which exists in two isomeric forms due to steric constraints within the planar carbene ligand.[3] However, when methylamine is added to hexakis(methyl isocyanide)iron(II) chelative addition occurs to produce the complex cation **2** (M = Fe; R = R′ = CH_3) which has been characterized by an X-ray diffraction study.[4] The formation of this complex probably proceeds through the normal attack of an amine on a coordinated isocyanide to yield the intermediate **1** (M = Fe; R = R′ = CH_3). Due to the close proximity of ligands in this six-coordinate intermediate, the carbene ligand can then function as a nucleophile toward a second isocyanide and effect ring closure to give **2**. Similarly ethylamine reacts with hexakis(methyl isocyanide)iron(II) to yield the chelate complex **2** (M = Fe; R = CH_3,

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