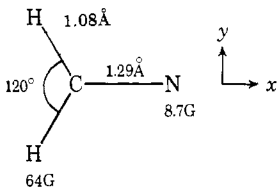
stant when R′ = H, and g values which are only slightly greater than the free-spin value of 2.0023. That these properties are consistent with the structure shown (I) is confirmed by an INDO calculation[4] on the model system II.



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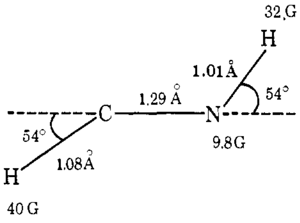

III

This indicates that most of the spin density (0.868) is in the p_y orbital on nitrogen and only a small fraction is in the carbon p orbitals, thus accounting for the small β-proton hfs. Satisfactory agreement of the calculated and observed α-proton and nitrogen hfs is also obtained (*cf.* structure II and Table I). The absence of appreciable spin density in the nitrogen p_x and p_z orbitals (0.001 and 0.047, respectively) shows that the nitrogen lone pair in II resides in a 2s orbital; therefore, no large g-value shift from free spin is expected.[5] Additional evidence in favor of structure I is the excellent agreement between our α-proton and nitrogen hfs and the values reported by Cochran, *et al.*,[3] for the H_2CN radical in argon.

An obvious alternative structure for radicals exhibiting a large proton hfs is III. This possibility is ruled out by (a) total energy considerations for several variations of III, including both *syn* and *anti* forms; (b) poor agreement between calculated and observed α-proton hfs; and (c) observation of small β-proton coupling constants. On this basis the structure I is preferred for all radicals listed in Table I.

It is apparent that the use of this unique matrix for photochemical studies on free radicals offers distinct advantages over conventional low-temperature matrix experiments;[6-8] namely, (a) the large temperature range over which the experiments may be performed,[1,2] (b) the straightforward analysis of the resulting isotropic epr spectra, and (c) the transparency of the matrix in wavelength regions of photochemical importance. Preliminary experiments have indicated that many other classes of free radicals in adamantane produced by X-irradiation yield results of similar photochemical interest. These results will be reported at a later date.

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Evidence against the Generality of the Ion-Pair Mechanism for Nucleophilic Substitution

Sir:

Recently, evidence has been reported[1-3] which suggests that certain nucleophilic displacements occur *via* attack of the nucleophile on a previously formed ion pair. Such evidence has been reported only for reactions in which the carbonium ion member of that pair would be stabilized by substituents. However, the proposal has been made[2] that *all* nucleophilic displacements from saturated carbon, including those involving primary and methyl substrates, occur *via* ion pairs, and that "Ion pairs have been established as substrates for nucleophilic attack; covalent, saturated carbon has not."[2]

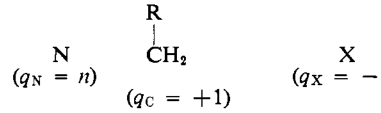
Studies in progress in these laboratories indicate that a full positive charge cannot be present on the central carbon of activated complexes for nucleophilic displacements on haloacetic acids; such a charge is required by an ion-pair mechanism. Covalent, saturated carbon therefore can and does act as a substrate for nucleophilic attack.

Consider a displacement in which nucleophile and leaving group are identical (*e.g.*, reaction 1, Table I). If the forward reaction passes through an ion pair prior to the rate-determining step, then the principle of detailed balance[4] requires that the reverse reaction pass through the same intermediate after its rate-determining step, and the symmetry of the reaction requires that such intermediates lie on both sides of the rate-determining transition state (eq 1). If direct

$$X^- + RX \rightleftarrows X^- + R^+X^- \underset{\text{step}}{\overset{\text{rate-determining}}{\rightleftarrows}} X^-R^+ + X^- \rightleftarrows XR + X^- \qquad (1)$$

attack on covalent, saturated carbon *never* occurs (as has been suggested),[2] then analogous arguments require that the rate-determining transition state also lie between ion-pair intermediates when the displacement is nonsymmetric. The activated complex would therefore resemble an ion triplet.

If the ion-pair mechanism were general, displacement by a nucleophile, N^{n+}, on a primary halide, RCH_2X, would thus proceed through a rate-determining transition state in which the central carbon of the activated complex, I, carried a charge, q_C, of one protonic unit



$$\underset{(q_N = n)}{N} \qquad \underset{(q_C = +1)}{\overset{\displaystyle R}{\overset{|}{CH_2}}} \qquad \underset{(q_X = -1)}{X}$$

I

and the charges, q_N and q_X, on N and X had values characteristic of free N^{n+} and X^-. If a fully covalent description of the transition state were correct, q_C would be zero and the sum, $q_N + q_X$, would be one

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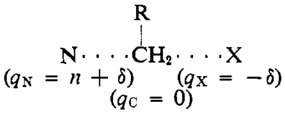
Table I. Observed and Predicted Transition State Acidities for Reactions at 65°

Reaction	$pK_a^{\ddagger\,a}$ (obsd)	$pK_a^{\ddagger}$ predicted for: Ion triplet (I, R = CO_2H)	Covalent (II, R = CO_2H)
$Br^- + BrCH_2CO_2H$	4.79 (CO_2H)[b]	<3.6	4.4 ± 0.5 (δ = 0.5)[c]
$HO^- + BrCH_2CO_2H$	4.36 (CO_2H)[b]	<3.0	4.9 ± 0.5 (δ = 0.5)[d]
$H_2O + BrCH_2CO_2H$	3.16 (CO_2H)[b]	<1.6	3.14[e] (δ = 0)[f]
$H_2O + BrCH_2CO_2H$	11.33 (H_2O)[b]	<9.6	11.1 ± 0.5 (δ = 0)[g]
$H_2O + BrCH_2CO_2^-$	12.54 (H_2O)[b]	<11.0	12.5 ± 0.5 (δ = 0)[g]

[a] Calculated from k for the tabulated reaction and k for the reaction involving the conjugate base of the tabulated reactant. [b] Functional group in the activated complex to whose ionization $pK_a^{\ddagger}$ refers. [c] Required by symmetry. [d] Predicted value of $pK_a^{\ddagger}$ is insensitive to δ due to cancellation of effects due to the CO dipole and to the negative charge. [e] Value for unperturbed $BrCH_2CO_2H$. [f] Predicted value of $pK_a^{\ddagger}$ is too low if δ is assumed large enough to produce a significant CO dipole. [g] Predicted value of $pK_a^{\ddagger}$ is too low if any significant positive charge is present on H_2O.

unit more positive than in I; such a structure is shown in II, where δ measures the C–N bond order.



$$\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{N}\cdots\cdots\mathrm{CH_2}\cdots\cdots\mathrm{X} \\ (q_\mathrm{N} = n + \delta) \quad\quad (q_\mathrm{X} = -\delta) \\ (q_\mathrm{C} = 0) \end{array}$$

II

It has been shown[5,6] that rate data for pairs of reactions in which the substrates differ only in whether or not they are protonated may be analyzed to obtain the value of pK_a for the activated complex in the reaction of protonated substrate. In general, if k_{HS} and k_S are rate constants observed for reaction of protonated and unprotonated substrate then

$$pK_a^{\ddagger} = pK_{HS} + \log (k_{HS}/k_S) \tag{2}$$

where pK_{HS} is pK_a for the initial state reactant, HS. In the experiments considered here, each pair of substrates is composed either of haloacetic acid and the corresponding haloacetate ion or of water and hydroxide ion; $pK_a^{\ddagger}$ thus measures the acidity either of the carboxyl proton or of the water protons in the activated complex.

Rate constants for the symmetric halide exchanges were taken from the literature.[7] Other rate constants were measured in these laboratories. All data refer to reactions in dilute aqueous solutions; all pK_a values were corrected to a reference state of zero ionic strength using the Davies equation.[8] Rate constants for the reactions of undissociated haloacetic acids with hydroxide ion were estimated from the corresponding rates observed for haloacetamides.

Methods for predicting the effects of charged and dipolar substituents on acid strength are well known. Both empirical correlations[6b,9,10] and direct electrostatic calculations[11–13] have been used, and the uncertainties in such predictions are significantly smaller than the differences between the pK_a values predicted for structures I and II. Table I lists values of $pK_a^{\ddagger}$ implied by the rate constants observed for hydrolysis and bromide exchange reactions of $BrCH_2CO_2H$ and $BrCH_2CO_2^-$. Also tabulated are pK_a values predicted for structures I and II (CCX and CCN angles of 90°, CX and CN distances for I calculated from the bond orders by Pauling's rule,[14] and for II set equal to the corresponding noble gas two-atom cluster distance).[15]

For example, consider $Br^{-1/2}CH_2(CO_2H)Br^{-1/2}$ (II (δ = 0.5), line 1, Table I). At 65°, CH_3CO_2H has pK_a = 4.92;[16] $(CH_3)_2CHCO_2H$ has pK_a = 4.98,[16] implying that steric hindrance by Br will not significantly affect $pK_a^{\ddagger}$. A model for the effect of the negative charge on Br is ΔpK = 2.6 for $HSeCH_2CO_2H$ *vs.* $^-SeCH_2CO_2H$;[17] correction for the difference in geometry between this model and II gives $\Delta pK^{\ddagger}$ = 3.3. Known values of dipole moments[18] and their variations with bond stretching[19] together with the observed effects of carbon–halogen dipoles at varying distances and angles on the acidities of carboxylic acids imply $\Delta pK^{\ddagger} = -3.7$ for the effect of the two CBr dipoles. Summing these estimates gives $pK_a^{\ddagger}$ = 4.5 ± 0.5; the uncertainty is estimated from the scatter observed when similar methods are used to predict acidities of compounds whose pK_a's are known.

Uncertainties are greater when predicting acidities for ion triplets, I. However, an upper bound on $pK_a^{\ddagger}$ can be assigned. For example, consider $Br^-C^+H_2(CO_2H)Br^-$ (I, line 1, Table I). Assuming that the effective dielectric constant, D_E, controlling transmission of the effect of the negative charges on bromide is as low as that for a covalent halo acid, that the D_E controlling transmission of the effect of the positive charge on carbon is as high as that for a charge on a terminal group, and that no CBr bond dipoles exist, then $pK_a^{\ddagger}$ = 3.6. More realistic estimates of any of those effects would result in lower estimates of $pK_a^{\ddagger}$.

In summary, $pK_a^{\ddagger}$ values observed for hydrolyses and bromide exchange reactions of $BrCH_2CO_2H$ and $BrCH_2CO_2^-$ (Table I) are all within the expected uncertainty of predictions for entirely covalent transition states and are all 1–2 pK units higher than the highest possible values for ionic transition states.[20]

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Since $\delta \approx 0$ for simple hydrolysis, an intermediate with no covalent bond to H_2O could be present; however, the CBr bond could not be ionic. Although all tabulated reactions have X = Br, qualitatively identical conclusions result when X = F, Cl, I.

Acknowledgment. We wish to express our gratitude to the National Science Foundation (Grants GP-7488, GP-13513) for financial support of this research.

(20) Small charges on the central carbon such as are present in conventional descriptions of S_N2 activated complexes (*e.g.*, J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 170) are consistent with the observed $pK_a^{\ddagger}$ values; charges of the magnitude required by an ion-pair mechanism are not. Further work may allow quantitative assignment of charges from $pK_a^{\ddagger}$ values.

(21) National Science Foundation Graduate Fellow, 1968–1969.

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The Degenerate [3,3]Sigmatropic Shift of Acetyl Peroxide

Sir:

Almost invariably, the [3,3]sigmatropic shift[1] of a 1,5-diene (the Cope rearrangement) predominates over its two potential competitors: [1,3] shift of either allyl moiety or homolytic cleavage into two such fragments[2] (Figure 1, X = CH_2). Current understanding of this preference is as yet less useful in heteroatomic systems. There, inversion of configuration is more difficult to detect; profound thermodynamic biases are more common.[2d–4]

To avoid the latter problem, one need only demand a choice among three such mechanisms in a degenerate transformation, here that of the π-isoelectronic diacyl peroxide (Figure 1, X = O). In this way we now demonstrate the [3,3]sigmatropic path to be the dominant (though not exclusive) one for the scrambling of carbonyl and peroxidic oxygens in acetyl peroxide. While confirming a prior speculation,[5] this too shifts the focus of current experimental disagreement.[6]

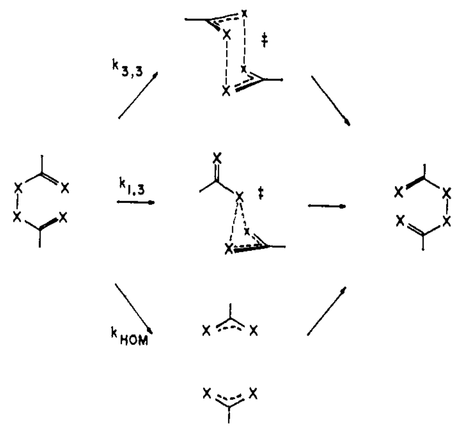

Figure 1. Competing mechanisms for a degenerate transformation.

Acetylcarbonyl-^{18}O peroxide was prepared from acetonitrile and "10%" enriched $H_2{}^{18}O$ by wholly conventional means.[7] Recrystallized first from ether and then from its solutions in isooctane and cumene, its 0.1 *M* solutions were found to be contaminated by less than 0.002 *M* ether (by gas chromatography) and by less than 0.001 *M* acetic acid (by infrared). The two peroxidic oxygen atoms could be converted intact to those of molecular oxygen in over 90% yield by the sequence: alkaline hydrolysis, acid hydrolysis, and Ce^{IV} oxidation. The expected[8] retention of isotopic integrity throughout both synthesis and degradation paths was confirmed by the identity (within 0.5%) of the 34/(33 + 32) *m/e* ratios of O_2 derived from enriched initial peroxide, from isotopically normal peroxide degraded in 1.5% ^{18}O enriched media, or from a commercial cylinder.

Corresponding degradation of partially decomposed acetyl peroxide, recovered from its cumene or isooctane solutions at 44.4 or 55.1°, provided O_2 whose increasing 34/32 and 36/34 *m/e* ratios (R_1 and R_2) were fitted to eq 1–4[9] by a nonlinear least-squares program.[10] The two experimentally distinguishable scrambling rate constants, λ_{TS} ("totalsc rambling")

$$R_1 = N_1/(1 - N_1 - N_2) \tag{1}$$

$$R_2 = N_2/N_1 \tag{2}$$

$$N_1 + 2N_2 = (c + p) - (c - p)e^{-\lambda_{TS}t} \tag{3}$$

$$N_2 = [(c + p)^2/4] - [(c^2 - p^2)/2]e^{-\lambda_{TS}t} + [(c - p)^2/4]e^{-\lambda_{RS}t} \tag{4}$$

and λ_{RS} ("random scrambling"), listed in Table I, are related by Figure 2 to the three possible mechanistic hypotheses.[11] In this way, exclusive dom-

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(3) Such systems might well also lie beyond the reach of otherwise useful approximation. *Cf.* M. J. S. Dewar, *Tetrahedron, Suppl.*, **8** (I), 75 (1966).

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(10) Details of both the mass spectral analysis and the statistical evaluation of its results may be found in the Ph.D. thesis of H. A. Judson, Cornell University, Ithaca, N. Y., Jan 1970, and will be elaborated in the full publication.

(11) The important alternative, an irreversible decomposition that entirely bypasses the acetoxy radical pair,[12] *is implicitly* included as the kinetically indistinguishable consequence of $f_R = 0$. Less plausible scrambling alternatives that require bimolecular intervention of free acetoxy radicals are ignored in view of the general consensus[6,13] that such radicals never escape their cage of birth.

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