the formalism of section 2 can be applied. Since H_{RP} commutes with F^2 and with the components of $\mathbf{F}$

$$[H_{RP},F^2] = 0 \quad [H_{RP},\mathbf{F}] = 0 \tag{A3}$$

the eigenstates of the radical pair can be characterized by F and M (M is the eigenvalue of F_z); the elements of the eigenvector matrix $\mathbf{T}$ (eq 5) are essentially Clebsch–Gordon coefficients. The matrix $\mathbf{Q}^P$ appearing in eq 11 becomes $\mathbf{Q}^P = \mathbf{E}_S \otimes \mathbf{I}$ ($\mathbf{I}$ is the unit matrix of order L) and therefore eq 18 now reads

$$V^P{}_{\nu l} = T_{1\nu',l} \tag{A4}$$

As a result, we have for the population of state $|1\nu'\rangle = |00KM_K\rangle$ in the case of a S precursor (*cf.* eq 24)

$$P^S{}_{\nu'} = \lambda(p - m\sum_{r'}\sum_{l,j} T_{1r',l}T_{1r',j}T_{1\nu',l}T_{1\nu',j} \times \sqrt{2\pi\omega_{lj}}) \tag{A5}$$

the Clebsch–Gordon coefficient $T_{1\nu',l} = \langle 00KM_K|FM\rangle$ has nonzero values for $M = M_K$, $F = K$, which restricts the sum over l and j to states with the same K and M_K. However, the coefficients $\langle 00KM_K|KM_K\rangle$ are all equal to unity[30] and therefore do not depend on M_K. Furthermore, ω_{jl} can be written

$$\omega_{jl} = |\omega_j - \omega_l| = |(H_{RP})_{jFM} - (H_{RP})_{lF'M'}| = |(H_{RP})_{jKM_K} - (H_{RP})_{lKM_K}| \tag{A6}$$

By using the fact that H_{RP} commutes with the components of $\mathbf{F}$ (eq A3) it is easy to show[31] that the diagonal matrix elements $(H_{RP})_{jKM_K}$ are independent of M_K. Thus the populations $P^S{}_{\nu'}$ do not depend on M_K either and are all equal within a K manifold. Since we have shown that the polarization from S and T precursors is opposite (eq 27), the same will hold in the case of a T precursor.

(30) A. Messiah, "Quantum Mechanics," Vol. II, North-Holland Publishing Co., Amsterdam, 1961, p 1058.
(31) *Cf.* ref 30, p 569.

Chemically Induced Dynamic Nuclear Polarization. XI. Thermal Decomposition of Acetyl Peroxide

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Abstract: A CIDNP study has been made of the thermal decomposition of acetyl peroxide and of carbon-13 and deuterium-substituted analogs. Proton, carbon-13, and deuterium CIDNP spectra have been recorded and are compared with computer simulations. The spectra can be accommodated with formation of acetoxy radicals, which decarboxylate rapidly to give methyl radicals. Net polarization in the geminate recombination products, methyl acetate and ethane, is probably due to singlet–triplet (T_0) transitions in the methyl–acetoxy radical pair (memory effect). In the case of the substituted acetyl peroxides, most of the ethane polarization arises from the methyl radical pairs. Applying a quantitative theory developed previously (part IX) for the case of reactions that compete with geminate recombination, it is found that (i) the absolute magnitude of the polarization enhancement, (ii) the ratio of the polarizations of methyl acetate and ethane, and (iii) the ratio of contributions from methyl–methyl and methyl–acetoxy radical pairs are compatible with a rate constant for the decarboxylation of the acetoxy radical in the range 2–3 × 10^9 sec^{-1}.

1. Introduction

The decomposition of acetyl peroxide (AP) is one of the most extensively investigated homolytic reactions. We have therefore choosen to study this reaction with nmr[2] in order to test current theories of CIDNP and to see whether nuclear polarization can help to answer some of the remaining questions concerning the reaction mechanism.

In most solvents the thermal decomposition of AP, $CH_3C(=O)OOC(=O)CH_3$, follows first-order kinetics with a rate constant very similar to a number of other acyl peroxides.[3] This has been taken as evidence[4] for the fact that the primary step is formation of a pair of acetoxy radicals by simple O–O bond scission; this is substantiated by a study of oxygen and deuterium isotope effects.[5] Szwarc and coworkers[4] suggested that methyl acetate and ethane were formed by a "cage" reaction, following decarboxylation of the very unstable acetoxy radical. This was inferred from their observation that these products were always formed in solution but not in the gas phase. ^{18}O scrambling found in both peroxide[5a] and methyl acetate[5a,6] from specifically labeled AP supports the intermediacy of short-lived acetoxy radicals. Cage recombination of acetoxy radicals may be responsible for the observed viscosity dependence of the overall decomposition rate.[7] Recent

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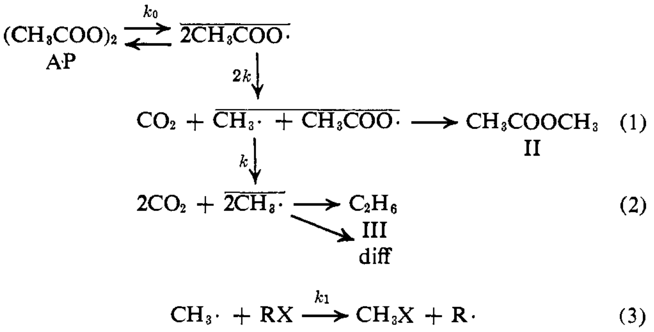
(2) (a) Presented in part at the CIDNP symposium of the American Chemical Society meeting in Houston, Texas, Feb 1970. (b) A preliminary account for this work was given in part I: R. Kaptein, *Chem. Phys. Lett.*, 2, 261 (1968).
(3) R. C. P. Cubbon, *Progr. React. Kinet.*, 5, 29 (1970).
(4) (a) M. Szwarz in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 153; (b) A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, 77, 3486 (1955); (c) L. Herk, M. Feld, and M. Szwarc, *ibid.*, 83, 2998 (1961).
(5) (a) J. W. Taylor and J. C. Martin, *ibid.*, 89, 6904 (1967); (b) T. Koenig and R. Cruthoff, *ibid.*, 91, 2562 (1969).
(6) T. Kashiwagi, S. Kozuka, and S. Oae, *Tetrahedron*, 26, 3619 (1970).
(7) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962).

work[8] has shown that ^{18}O scrambling in the peroxide itself is also partly due to [3,3] and possibly [1,3] sigmatropic rearrangements in AP, which are, however, of no concern for us here.

Thus, from these and other studies a mechanistic picture has emerged for the thermal decomposition of AP in "inert" solvents, which is now favored by most workers, and which is summarized in Scheme I. RX denotes the solvent or some other substrate, to be specified later on. The bars indicate radical pairs with correlated electron spins, derived from a common parent molecule. The rate constant, k, for the decarboxylation of the acetoxy radical has been estimated to be of the order 10^9–10^{10} sec^{-1} by Szwarc.[4] Eirich and co-workers,[7] applying a theoretical model for geminate recombination, have found a value $k = 1.6 \times 10^9$ sec^{-1} at 60° and an activation energy of 6.6 kcal/mol from product studies. Thus the time scale of the decarboxylation process is of the same order as that of geminate recombination,[9] which renders this system particularly interesting from the point of view of CIDNP, since effects of the successive pairs will be observable.

Scheme I



$$\begin{tikzcd}
\underset{\mathrm{AP}}{\mathrm{(CH_3COO)_2}} \arrow[r, shift left, "k_0"] & \overline{\mathrm{2CH_3COO\cdot}} \arrow[l, shift left] \arrow[d, "2k"] & \\
& \mathrm{CO_2} + \overline{\mathrm{CH_3\cdot} + \mathrm{CH_3COO\cdot}} \arrow[r] \arrow[d, "k"] & \underset{\mathrm{II}}{\mathrm{CH_3COOCH_3}} \quad (1) \\
& \mathrm{2CO_2} + \overline{\mathrm{2CH_3\cdot}} \arrow[r] \arrow[dr] & \mathrm{C_2H_6} \quad (2) \\
& & \underset{\mathrm{diff}}{\mathrm{III}}
\end{tikzcd}$$

$$\mathrm{CH_3\cdot} + \mathrm{RX} \xrightarrow{k_1} \mathrm{CH_3X} + \mathrm{R\cdot} \quad (3)$$

In preceding parts[10] we have incorporated Noyes theory of geminate diffusive recombination[9,11] into a previously given formalism[12] of the radical pair theory of CIDNP. This theory has been independently proposed by Closs.[13] Competitive reactions have been treated in part IX, within the framework of the diffusion model, and the case of AP has already been shortly discussed as an example.[10b] It will be shown presently that CIDNP spectra obtained during thermolysis of AP are in accordance with the reactions of Scheme I.

As the products of AP decomposition have single line nmr spectra, we have also studied acetyl peroxides, substituted with magnetic isotopes, in which cases CIDNP spectra contained more information. Thus apart from normal AP, we will discuss 2,2′-^{13}C-acetyl peroxide (55% enriched in the methyl carbon), 2,2′-dideuterioacetyl peroxide and hexadeuterioacetyl peroxide. In addition to proton spectra, some carbon-13 and deuterium CIDNP spectra will be presented.

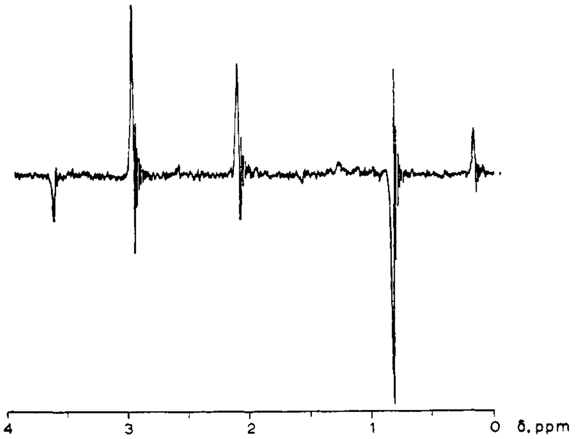


Figure 1. 60-Mc spectrum taken during decomposition of 0.1 M AP in hexachloroacetone at 110°.

2. Acetyl Peroxide (AP)

2.1. CIDNP Spectra. CIDNP during thermolysis of AP in hexachloroacetone (HCA) and in thiophenol has been reported in part I. Bargon and Fischer have discussed the reaction of AP in dimethyl phthalate.[14] A 60-Mc spectrum of a 0.1 M solution of AP (δ 2.11 ppm) in HCA at 110° is shown in Figure 1. Emission (E) is observed for ethane (δ 0.83 ppm) and methyl acetate (OCH_3, 3.54 ppm) and enhanced absorption (A) for methyl chloride (δ 2.94 ppm) and methane (δ 0.18 ppm). At higher temperatures the E signal at 1.60 ppm becomes more clearly visible; we have tentatively assigned this line to 1,1,1,3,3-pentachlorobutan-2-one, on the analogy with results for isopropyl and *tert*-butyl radicals, where A for pentachloroacetone has been observed. This E line can be observed in Figure 2. This fishbone shows the development of this system in time. The spectrum has been run at 120° on a Varian HA-100 spectrometer, by repeatedly scanning a region of 4.8 ppm with a sweep rate of 25 Hz/sec. The increase of the E and A curves represent the warming up of the sample in the probe. The decrease results from a slower reaction due to consumption of AP.

The opposite behavior of recombination and transfer reaction products (noted already in I) was rather mysterious at the time but is a natural consequence of the radical pair mechanism. As the acetoxy radical most probably has a larger g factor than the methyl radical, the theory predicts E for methyl acetate, when formed from the methyl/acetoxy radical pair (*cf.* Scheme I), and A for products from radicals escaping from recombination, *viz.*, methyl chloride and methane. Methane might be formed by H abstraction from pentachloroacetone (about 1% or less present in HCA) or from AP.

2.2. Origin of the Ethane Polarization. The E effect for ethane cannot be due to S–T_0 mixing in the methyl radical pair, because no net effects can arise from pairs of equivalent radicals. In order to ascertain the origin of the ethane emission, we have studied its dependence on peroxide concentration. The results are presented in Figure 3.

The linear dependence is expected for a polarization mechanism associated with geminate recombination but

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(8) M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, **92**, 4119 (1970).

(9) (a) R. M. Noyes, *ibid.*, 77, 2042 (1955); (b) *ibid.*, **78**, 5486 (1956).

(10) (a) Part VIII: R. Kaptein, *ibid.*, **94**, 6251 (1972); (b) part IX: *ibid.*, **94**, 6262 (1972).

(11) *Cf.* F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970).

(12) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969).

(13) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

(14) J. Bargon and H. Fischer, *Z. Naturforsch.*, *A*, **23**, 2109 (1968). The emission line at 0.79 ppm reported in this paper has been erroneously assigned to methane (instead of ethane).

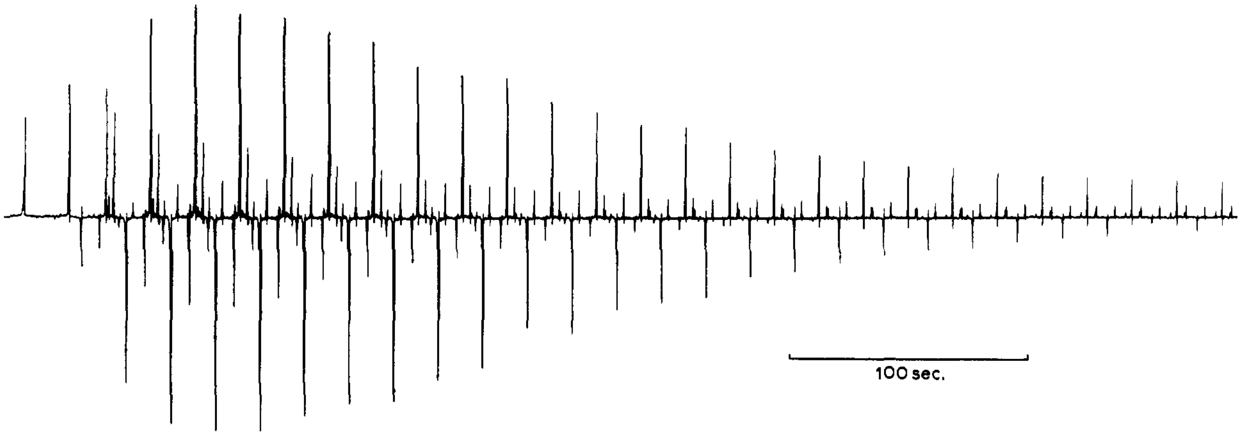

Figure 2. Time development of the polarization during decomposition of AP in HCA at 120°, obtained by repeatedly sweeping through a region of 4.8 ppm.

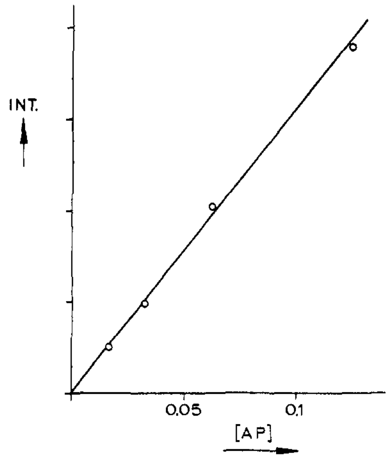

Figure 3. Maximum intensity of ethane emission (arbitrary units) *vs.* concentration of AP (in mol/l.) during decomposition in HCA.

could not be explained by other mechanisms involving cross-relaxation and combination of free methyl radicals.

A further indication is provided by comparison of ^1H spectra run at 100, 60, and 15.1 Mc. The ratio of *E* intensities of methyl acetate and ethane was found to be essentially constant for the different fields. Thus we are led to the conclusion that polarization of methyl acetate and that of ethane have a common origin: $S\text{-}T_0$ mixing in the methyl/acetoxy radical pair. This phenomenon was called a "memory effect" in part IX, since polarization due to $S\text{-}T_0$ transitions in pair 2 (methyl/acetoxy) shows up in products of pair 3 (methyl/methyl). This can be understood qualitatively as follows: $S\text{-}T_0$ transitions in pair 2 are favored for methyl radicals with $M_i > 0$ (*z* component of nuclear spin). As during decarboxylation the electron spins (and nuclear spins) will not change, there will be born more methyl radical pairs with $M_i < 0$ in the singlet state, giving rise to emission for ethane.

A disproportionation reaction of the type

$$\overline{CH_3\cdot + CH_3COO\cdot} \longrightarrow C_2H_6 + CO_2 \qquad (4)$$

would give similar polarization. It cannot be excluded on the basis of the spectra of Figures 1 and 2 (see, however, section 3).

2.3. Enhancement Factors. The results for AP in HCA are summarized in Table I. Yields were determined by integration of the nmr spectrum after decomposition in a sealed tube and represent peak areas of the various products related to that of AP before reaction. "T_1" is the characteristic decay time for the polarization, determined by saturation recovery of the *polarized* lines, during the reaction. In this way both spin-lattice relaxation and escape of gaseous products from the sample are accounted for in "T_1."

Table I. Decomposition of 0.1 *M* AP in HCA at 110° (100 Mc)

Products	δ, ppm	Yield, %[a]	"T_1," sec[b]	V'[c]
AP	2.11 N[d]			
Methyl acetate (OCH_3)	3.54 E	32	9	−44
(CCH_3)	1.96 N			
Ethane	0.83 E	5	11	−168
Methyl chloride	2.94 A	41	7	+192
Methane	0.18 A	6		
Pentachlorobutanone[e]	1.60 E	<0.5		
Acetic acid	2.02 N	11		
Acetic anhydride	2.16 N	3		
Other products		2		

[a] Determined from nmr integration after decomposition in sealed tube; estimated relative error ±10%. [b] Determined from saturation recovery during decomposition. [c] Calculated from eq 5; estimated error ±20%. [d] N, not enhanced. [e] Tentative assignment.

V' is the enhancement factor per molecule AP decomposed introduced previously[10]; it is simply related to experimental quantities

$$V' = (I - I^0)/I(AP_{t'})T_1k_0 \qquad (5)$$

where the observed intensity, I, the thermal equilibrium intensity, I^0, and the intensity of the precursor, $I(AP_{t'})$, are measured at time t', the time of maximum enhancements. The rate constant for AP decomposition[15] is $k_0 = 2.5 \times 10^{-3}$ sec^{-1} at 110°. It was necessary to allow for I^0 only in the case of methyl acetate, where I^0 has been set equal to the intensity of the acetate CH_3 group. Since only one CH_3 fragment is responsible for

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(15) The apparent rate constant (from disappearance of the AP signal) has been corrected for an estimated 20% cage return of acetoxy radicals.

the polarization,[16] half the intensity of the AP signal has been taken for $I(\mathrm{AP}_{t'})$.

It can be noted that the yield of ester is much larger than that of ethane, while the reverse is true for the polarization. It is interesting to compare the experimental ratio of the enhancement factors for methyl acetate and ethane, $V'_{\mathrm{II}}/V'_{\mathrm{III}}(\mathrm{exp}) = 0.26$, with predictions of the theory. In part IX a calculation has been made for a one-proton pair, with parameters pertaining to this case. For k (rate of decarboxylation) between 10^9 and 10^{10} sec^{-1}, it was found that $V'_{\mathrm{II}}/V'_{\mathrm{III}}$(theor) $\sim$0.17–0.10. If the experimentally observed ester yield is used ($P_{\mathrm{II}} = 0.32$ in eq 24 of IX) these values become 0.27–0.13. For $k = 2 \times 10^9$ sec^{-1} the enhancement factor calculated for the ester would be $V'_{\mathrm{II}} = -50$ (close to the observed value of -44) and the calculated ratio $V'_{\mathrm{II}}/V'_{\mathrm{III}}$(theor) = 0.19, in reasonable agreement with the observed 0.26.

The intensity of the methyl chloride A line depends on k_1 (rate constant for chlorine abstraction from HCA by methyl radicals) and also on the relaxation time of methyl radicals. The rate constant k_1 has been measured[18] and would have a value $k_1 = 2 \times 10^4$ l./mol sec at 110°. If methyl radicals disappear predominantly by reaction with the solvent, their lifetime would be $(k_1[\mathrm{HCA}])^{-1} = 7.7 \times 10^{-6}$ sec. Relaxation times of radicals are usually in the range 10^{-5}–10^{-4} sec (longer times have even been inferred from CIDNP spectra[19,20]), so that the lifetime of the methyl radical could well be shorter than its relaxation time, giving polarization of about the same magnitude, but opposite to that of ethane and methyl acetate.

The E effect attributed to pentachlorobutanone deserves some comment. This effect would be compatible with recombination of singlet-correlated methyl/pentachloroacetonyl radical pairs (we measured $g_{\mathrm{pentachloroacetonyl}} = 2.0080$ by esr)

$$\overline{2\mathrm{CH_3}\cdot} \xrightarrow{\mathrm{HCA}} \overline{\mathrm{CH_3}\cdot + \mathrm{CCl_3COCCl_2}\cdot} \longrightarrow \mathrm{CCl_3COCCl_2CH_3} \quad (6)$$

Since this pair is formed after about 4 μsec (on the average), we would have another example of long-time spin-correlation effects of the type discussed in IX. Formation of acetic acid and acetic anhydride (as indicated by nmr and glc) is somewhat surprising. The mechanism by which these products are formed is not known.

3. 2,2′-^{13}C-Acetyl Peroxide (^{13}C-AP)

So far CIDNP spectra were in reasonable agreement with the reactions of Scheme I, but other possibilities were not excluded. For instance, reaction 4 might also account for the ethane emission. The results of ^{13}C-AP show that this cannot be an important route to ethane.

3.1. ^{1}H Spectrum. The 100-Mc ^{1}H nmr spectrum taken during decomposition of 0.22 M ^{13}C-AP in HCA at 110° is shown in Figure 4a. As the ^{13}C enrichment of the methyl carbon atom is only 55 ± 1% (from nmr), the same lines appear as in Figure 1 (*cf.* Table I) due to products of $^{12}\mathrm{CH_3}\cdot$ radicals. In addition, lines belonging to products of $^{13}\mathrm{CH_3}\cdot$ radicals appear. Since the ^{13}C nucleus has spin $I = {}^1/_2$ the spectra of methyl acetate, methyl chloride, peroxide, and methane, containing $^{13}\mathrm{CH_3}$ fragments, consist of doublets flanking the ^{12}C species: methyl acetate (OCH$_3$), $J_{\mathrm{CH}} = 146$ Hz, $E + E/A$; methyl chloride, $J_{\mathrm{CH}} = 150$ Hz, $A/E + A$; ^{13}C-AP, $J_{\mathrm{CH}} = 131$ Hz; methane, $J_{\mathrm{CH}} = 124$ Hz, $A/E + A$. From the ^{13}C-methyl acetate doublet (E lines with unequal intensities) the g factor of the acetoxy radical can be obtained. Calculations with an exchange integral $|J| = 5 \times 10^8$ radians/sec gave the best fit with $\Delta g = 0.0032 \pm 0.0002$ for the methyl/acetoxy radical pair, which implies $g_{\mathrm{acetoxy}} = 2.0058 \pm 0.0002$ ($g_{\mathrm{methyl}} = 2.0026$, *cf.* ref 21). The g factor of this very unstable radical will not easily be obtained from esr.

The spectrum of ethane[22] in the region 0–1.8 ppm is more complex because of coupling between nuclei of both CH$_3$ fragments. Furthermore, apart from normal ^{12}C-ethane, two ethanes are formed: $^{12}\mathrm{CH_3}$–$^{13}\mathrm{CH_3}$ and $^{13}\mathrm{CH_3}$–$^{13}\mathrm{CH_3}$. The nuclear coupling constants[22] are: $J_{\mathrm{CH}} = 125.0$ Hz, $J_{\mathrm{CCH}} = -4.5$ Hz, $J_{\mathrm{CC}} = 34.6$ Hz, and $J_{\mathrm{HCCH}} = 8.0$ Hz. Computer simulations have been made, following the precedures given in VIII.

The simulation of Figure 4a is a superposition of both ^{13}C containing ethanes and has been calculated with the hf parameters of the pairs $^{12}\mathrm{CH_3}\cdot/^{13}\mathrm{CH_3}\cdot$ and $2^{13}\mathrm{CH_3}\cdot$, $A_{\mathrm{H}} = -23.0$ G, $A_{^{13}\mathrm{C}} = +38.3$ G,[23] and with $|J| = 5 \times 10^8$ radians/sec. It is clear from Figure 4a that the methyl radical pair is responsible for most of the ethane polarization, in accordance with reaction 2 of Scheme I. However, the E effect of normal ^{12}C-ethane is thought to arise from the methyl/acetoxy radical pair (memory effect) and indeed, when polarization from this pair is superimposed,[24] the agreement with experiment becomes even better (Figure 4b). It should be noted that two methane lines (at 0.80 and 0.18 ppm) and a ^{13}C-AP line (1.43 ppm) overlap with the ethane spectrum.

The best fit is obtained when the ratio of contributions from the pairs $2\mathrm{CH_3}\cdot$ and $\mathrm{CH_3}\cdot/\mathrm{CH_3COO}\cdot$ is 1.9:1. On the basis of the theory given in part IX, one would predict that this ratio is rather sensitive to the value of k. For a simplified model,[25] the calculated ratio varies between 0.8 and 10, for k in the range 10^9–10^{10} sec^{-1}. The value 1.9 is obtained for $k = 3 \times 10^9$ sec^{-1}, which is very close to the value 2×10^9 mentioned above.

In order to obtain a good fit it was found to be necessary to use a ratio 68:32 for the contribution from

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(16) The hf coupling constant $A(\mathrm{CH_3})$ in the acetoxy radical is not known but will probably be comparable to $A(\mathrm{CH_3})$ in the 2-methyl allyl radical[17] (3.19 G), thus much smaller than $A_{\mathrm{H}} = -23$ G in the methyl radical.

(17) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(18) D. M. Tomkinson, J. P. Galvin, and H. O. Pritchard, *J. Phys. Chem.*, **68**, 541 (1964).

(19) G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 7229 (1970).

(20) M. Lehnig and H. Fischer, *Z. Naturforsch.*, *A*, **25**, 1963 (1970).

(21) H. Fischer, "Magnetic Properties of Free Radicals," Landolt-Börnstein, New Series, Group II, Vol. 1, K.-H. Hellwege, Ed., Springer-Verlag, West Berlin, 1965.

(22) (a) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962); (b) D. H. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

(23) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(24) Both ^{1}H- and ^{13}C-hf coupling constants of the methyl carbon in the acetoxy radical have been set equal to zero. Trial calculations with A_{H} and $A_{^{13}\mathrm{C}}$ of the order of 3 G did not change the spectrum significantly.

(25) The calculations have been performed for a one-proton pair with $\Delta g = -0.0032$ (for the methyl–acetoxy radical pair) and a two-nuclei pair (for the methyl radical pair) on the basis of eq 24 of IX. Other parameters used: $|J| = 5 \times 10^8$ radians/sec, $m' = 10^{-6}$ sec$^{1/2}$, $p = {}^1/_2$, $\lambda_{\mathrm{III}} = 1$, $P_{\mathrm{II}} = 0.32$ and the hf parameters of thc $^{13}\mathrm{CH_3}\cdot$ radical.

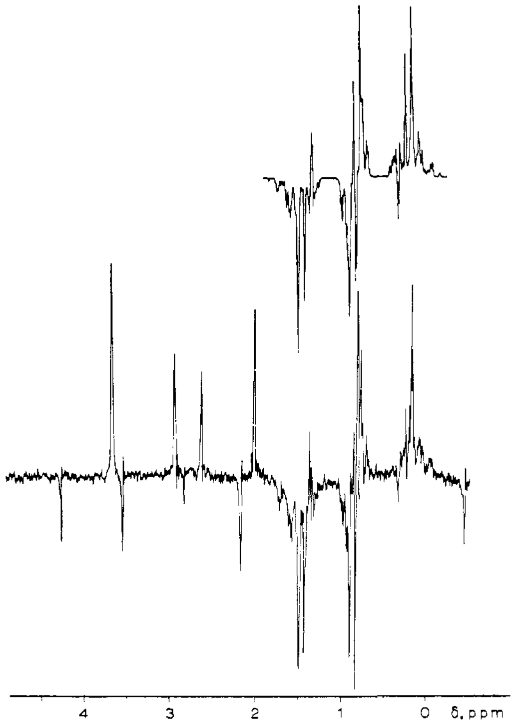

Figure 4a. 100-Mc ^1H spectrum of the decomposition of 0.22 *M* ^{13}C-AP (55% enriched) in HCA at 110°. A simulation of the ethane spectrum, calculated with the parameters of the methyl radical pair (see text), is shown on top.

Figure 4b. Simulation of the ethane ^1H spectrum from ^{13}C-AP. Contributions of polarization from the pairs $2CH_3\cdot$ and $CH_3\cdot/CH_3COO\cdot$ are superimposed in the proportion 1.9:1.

both ethanes ($^{12}C-^{13}C$:$^{13}C-^{13}C$) to the spectrum of Figure 4 (and also for the ^{13}C spectrum, Figure 5), instead of the statistically expected ratio 63:37. The discrepancy seems somewhat large to be explained by a kinetic isotope effect for the decarboxylation of the acetoxy radical, although this would be expected to give an effect in the right direction ($k_{12} > k_{13}$, *cf.* ref 26). We have not pursued this point further. For $^{13}CH_3Cl$, the pairs $2CH_3\cdot$ and $CH_3\cdot/CH_3COO\cdot$ contribute about equally to the spectrum. The relatively larger effect due to the last pair, as compared to the case of ethane, is to be expected, since in the "escape" product the net effects of methyl acetate must be balanced as well as those of ethane.

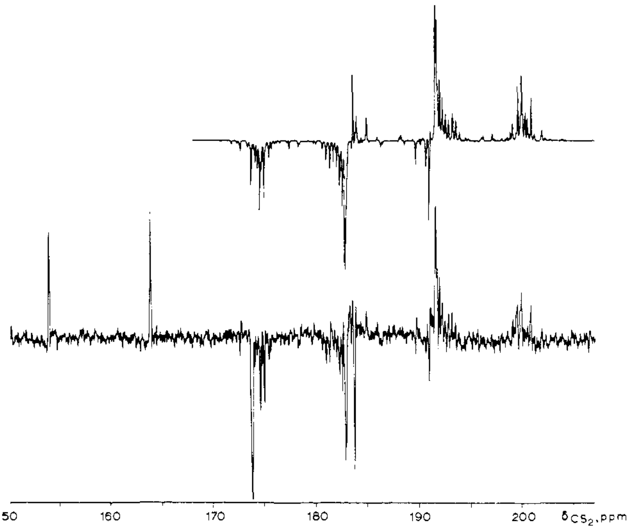

Figure 5a. 15.1-Mc ^{13}C spectrum of the decomposition of ^{13}C-AP in HCA at 124°. A simulated spectrum of the ethanes (polarization from the methyl radical pair) is shown on top.

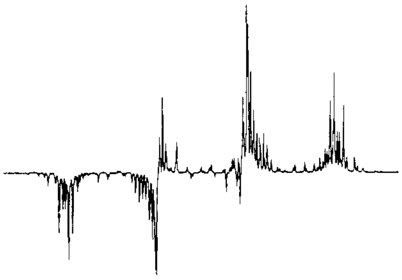

Figure 5b. Simulation of the ethane ^{13}C spectrum from ^{13}C-AP. Contributions of polarization from the pairs $2CH_3\cdot$ and $CH_3\cdot/CH_3COO\cdot$ are superimposed in the proportion 1.9:1.

3.2. ^{13}C Spectrum. The 15.1-Mc ^{13}C spectrum (H_0 = 14 kG) during decomposition of ^{13}C-AP in HCA at 124° is shown in Figure 5a. In order to obtain an acceptable signal-to-noise ratio, the reaction temperature was somewhat higher than in the case of the ^1H spectrum. Polarization is observed for methyl chloride and ethane. $^{13}CH_3Cl$ shows an *A*/*E* quartet centered around 169 ppm from CS_2 (lines at 154, 164, 174, and 184 ppm). Some *E* character is also present, as expected for this product.

The ethanes give rise to a complex spectrum centered around 187 ppm. The computer simulation of Figure 5a has been calculated with the same parameters as that of Figure 4a. Again, the polarization is almost completely accounted for by spin selection in the methyl radical pair. When the effect of the methyl/acetoxy radical pair is superimposed in the same proportion as used for the proton spectrum (1.9:1), the simulation does not change drastically (Figure 5b). The small *A* character is not observed experimentally. The reason may be a decrease of the decomposition rate near the end of the scan (~200 sec) due to the high temperature. Furthermore, the decarboxylation is probably somewhat faster at this temperature (124°), and consequently a ratio higher than 1.9:1 for the pairs $2CH_3\cdot$ and $CH_3\cdot/CH_3COO\cdot$ would be required.

3.3. 50/50 Mixture Enriched/Nonenriched AP. The AP system enabled us to perform an experiment, which proves unequivocally the radical pair nature of the polarization. At present this seems hardly necessary to prove, since there is abundant convincing evidence for it.

(26) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, Chapter 7.

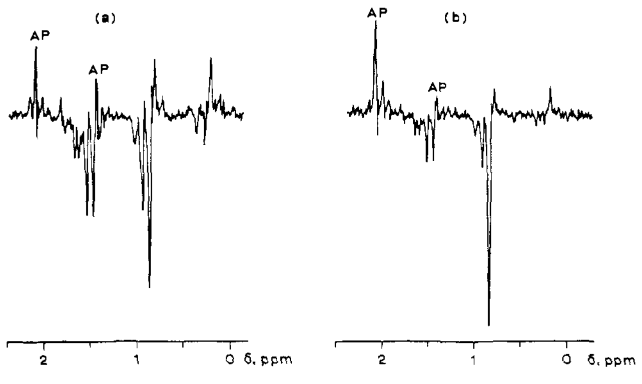

Figure 6. 100-Mc ^{1}H spectra of the decomposition of 0.22 M ^{13}C-AP in hexachlorobutadiene with CCl_3Br (a) and of a mixture of 0.11 M AP and 0.11 M ^{13}C-AP in the same solvent (b).

However, at the time when this experiment was carried out (1969) things were not yet so clear.

The ethane polarization, resulting from decomposition of 0.22 M ^{13}C-AP in hexachlorobutadiene, containing 0.5 M CCl_3Br (to suppress formation of methane), was compared with that from a similar solution containing 0.11 M AP and 0.11 M ^{13}C-AP. The CIDNP spectra were recorded under as nearly as possible identical conditions for both cases. The results are shown in Figure 6. The ratios, in which the contributions from three ethane polarizations are expected to change in the case of different polarization mechanisms, are presented in Table II.

Table II. Relative Amounts of Ethane Products Formed from 55% Enriched ^{13}C-AP and from a 50/50 Mixture AP/^{13}C-AP (55%), as Expected for "Cage" Recombination and for Random Combination of Methyl Radicals ("random")

	^{12}C–^{12}C	^{12}C–^{13}C	^{13}C–^{13}C
55% enriched ^{13}C-AP	20	50	30
50/50 mixture AP/^{13}C-AP "cage"	60	25	15
50/50 mixture AP/^{13}C-AP "random"	52	40	8

The expectations for a geminate recombination ("cage") process are compared with one in which *polarized* ethane would be formed by random encounters. Comparing Figures 6a and 6b, it can be observed that (i) intensities of the ^{13}C-containing ethanes in (b) are reduced by a factor $^1/_2$ as compared to (a), and (ii) relative intensities of lines belonging to different ethanes are unaltered (*e.g.*, lines of the "doublet" at 1.5 ppm belong to different ethane molecules). This is in perfect agreement with the second line of Table II. It shows, without using any theory of CIDNP, that the ethane polarization results from a "cage" process and rules out any mechanism acting in free methyl radicals, such as the original cross-relaxation mechanism.

4. Dideuterioacetyl Peroxide (D_2-AP)

Deuterium has a spin $I = 1$. The ratio of the nuclear g factors of ^{2}D and ^{1}H is $g_D/g_H = 0.154$. Therefore the coupling constants A_D (in the radicals) and J_{HD} (in the products) are smaller than the corresponding A_H and J_{HH} by a factor 6.5 ($A_D = -3.54$ in the $CH_2D\cdot$ radical[23]). Both ^{1}H and ^{2}D spectra have been examined. Deuterium chemical shifts (in ppm) are the same as for protons.

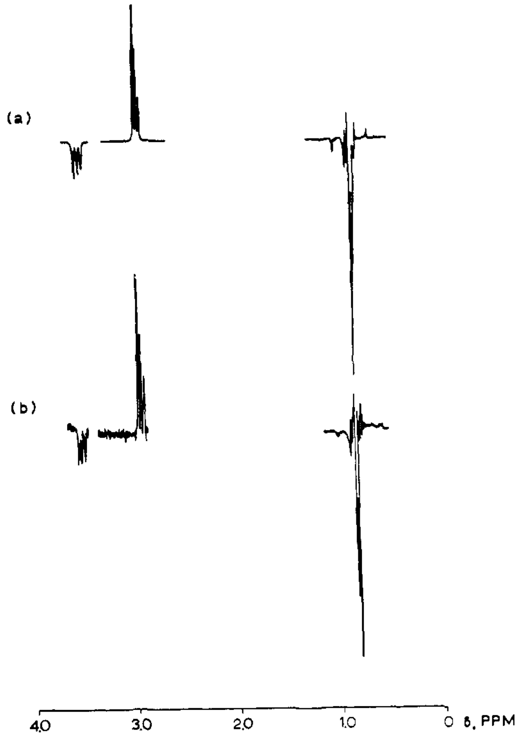

Figure 7. 60-Mc ^{1}H spectrum of the decomposition of D_2-AP in HCA at 110°

4.1. ^{1}H Spectrum. Figure 7 presents a 60-Mc ^{1}H spectrum obtained during decomposition of D_2-AP in HCA. Narrow triplets are observed for CH_2DCl ($J_{HD} = -1.7$ Hz, $A + A/E$) and for dideuteriomethyl acetate (OCH_2D, $J_{HD} = -2.5$ Hz, $E + E/A$). Both CH_2DCl and $^{13}CH_3Cl$ (Figure 4a) show A/E multiplet effects, the reason being that both the hyperfine coupling constant (A_D) and the nuclear spin coupling constant (J_{HD}) have changed sign (compared to $A_{^{13}C}$ and J_{HC}).

Again, the spectrum of 1,2-dideuterioethane is more complex. Nuclear coupling constants in CH_2D–CH_2D are: J_{HH}(vicinal) = +8.0 Hz, J_{DD}(vicinal) = +0.19 Hz, J_{HD}(geminal) = −1.6 Hz, and J_{HD}(vicinal) = +1.22 Hz. The simulated spectra of Figure 7a have been calculated with the same parameters as used in the previous sections (except for coupling constants involving ^{2}D). For CH_2DCl the ratio of the pairs $2CH_2D\cdot$ and $CH_2D\cdot/CH_2DCOO\cdot$ was 1:1 and for CH_2D–CH_2D it was 1.9:1. The good agreement with experiment shows that this case is consistent with the previous case of ^{13}C-AP.

4.2. ^{2}D Spectrum. Due to the quadrupole moment of the deuterium nucleus, the relaxation times of lines in ^{2}D spectra are somewhat shorter than in the corresponding ^{1}H spectra. Usually they lie in the range 0.5–5 sec,[27] which is not too short for deuterium polarization to be observed. The 15.4-Mc ^{2}D spectrum (H_0 = 23.5 kG) of the decomposition of ^{2}D-AP in HCA at 120° is shown in Figure 8a and a computer simulation of CH_2DCl (2.94 ppm) and CH_2D–CH_2D (0.83 ppm) in Figure 8b. Apart from the higher magnetic field the same parameters have been used as for the simulation of Figure 7. The more pronounced multiplet effect relative to the net effect in the ^{2}D spectrum as compared

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(27) J. A. Glasel, *J. Amer. Chem. Soc.*, **91**, 4569 (1969).

Figure 8. 15.4-Mc ^{2}D spectrum of the decomposition of D_2-AP in HCA at 120°.

with the ^{1}H spectrum (Figure 7) is well reproduced. This difference can be understood by considering the approximate formula, which describes relative CIDNP intensities (*cf.* eq 49 of VIII, strictly valid in the limit of large exchange integral $|J|$).

For the ^{1}H spectrum

$$\tfrac{1}{2}A_H(\Delta g\beta\hbar^{-1}H_0 + A_D M_D) \qquad (7a)$$

For the ^{2}D spectrum

$$\tfrac{1}{2}A_D(\Delta g\beta\hbar^{-1}H_0 + A_H M_H) \qquad (7b)$$

where both M_D and M_H take the values -1, 0, $+1$ (labeling the states of ^{2}D and of the protons respectively). The first terms in (7) represent the net effects and the second terms the multiplet effects. Since $A_D/A_H = 0.154$, it is clear that the multiplet effect will be *relatively* larger in the ^{2}D spectrum (Figure 8) than in the ^{1}H spectrum (Figure 7).

5. Hexadeuterioacetyl Peroxide (D_6-AP)

The 15.4-Mc ^{2}D spectrum resulting from the decomposition of D_6-AP in HCA at 120° is presented in Figure 9. This spectrum is very similar to the one of Figure 1 (*cf.* Table I), except for trideuteriomethane (CD_3H), which gives rise to a doublet in this case. The CD_3H signal (0.18 ppm) is rather large but disappears much faster than that of CD_3Cl (2.94 ppm). Unless there are large differences in relaxation times, this indicates that H-atom abstraction from pentachloroacetone (about 1% present) is much faster than Cl-atom abstraction from HCA.

6. Conclusions

On the basis of the reaction mechanism of Scheme I, radical pair theory is able to account for the observed CIDNP spectra during decomposition of acetyl peroxide and of ^{13}C-enriched and deuterated analogs. Ethane formation by reaction 4 and similarly formation of methyl acetate by disproportionation of acetoxy radicals, which has been considered[4]

$$2CH_3COO\cdot \longrightarrow CH_3COOCH_3 + CO_2 \qquad (8)$$

are not likely to be of major importance, if these reactions contribute at all.

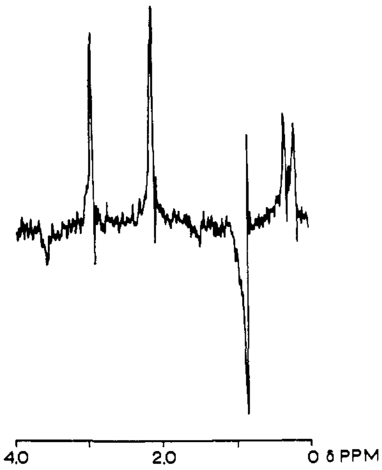

Figure 9. 15.4-Mc ^{2}D spectrum of the decomposition of D_6-AP in HCA at 120°.

A rate constant for the decarboxylation of acetoxy radicals, $k \sim 2\text{–}3 \times 10^9$ sec^{-1}, seems to be compatible with (i) the absolute enhancement of methyl acetate polarization, (ii) the ratio of polarizations of ester and ethane (memory effect), and (iii) the ratio of contributions from methyl and methyl/acetoxy radical pairs, in the case of ^{13}C and ^{2}D containing ethanes. This compares favorably with the value $k(110°) = 5 \times 10^9$ sec^{-1}, obtained by Eirich.[7]

7. Experimental Section

Reagents. Acetic anhydride, hexadeuterioacetic anhydride (98% enriched), and 2-^{13}C-acetyl chloride (55% enriched) were obtained commercially; 2,2′-dideuterioacetic anhydride was prepared[28] from ketene and D_2O (*cf.* ref 29). Solvents were distilled before use. Hexachloroacetone contained some pentachloroacetone as an impurity (1% or less).

Peroxides. Acetyl peroxide and hexadeuterio- and dideuterioacetyl peroxide were prepared from the anhydrides following the procedure of Price and Morita[30] (addition of Na_2O_2 and water to a solution of the anhydride in ether while keeping the temperature below 5°, washing the ethereal layer in aqueous $NaHCO_3$, and drying over Na_2SO_4). The synthesis of acetyl peroxide from acetyl chloride by this method, without special precautions, gave low yields of peroxide (10–15%). However, by varying the reaction conditions somewhat, the yield could be boosted to 80%. The following procedure was used for the preparation of 2,2′-di-^{13}C-acetyl peroxide. To a solution of 0.44 g of 2-^{13}C-acetyl chloride in 3.5 ml of ether, cooled to $-15°$, was added 0.45 g of Na_2O_2. Four drops of water were added and the mixture was stirred during 40 min at $-10°$. After adding 3 ml of chilled ether the solution was decanted and the ethereal layer was washed with 10% aqueous $NaHCO_3$ and with 5% NaCl solution and dried over $MgSO_4$. The yield was 80%, as determined by iodometric titration.[31]

Nmr Spectra. The 60-Mc spectrum of Figure 1 was recorded on a Varian A-60 spectrometer. The 60-Mc spectrum of Figure 7 and the 15.1-Mc ^{13}C spectrum (Figure 5) were run on a Varian DA-60; the 100-Mc ^{1}H spectra and the 15.4-Mc ^{2}D spectra on a Varian HA-100. In the case of the 100-Mc spectra sample tubes contained a capillary with H_2SO_4, for an internal lock signal. No lock signal

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(28) We thank Mr. R. L. C. Wijting for the preparation of this anhydride and of di- and hexadeuterioacetyl peroxide.

(29) F. I. Andersen, *Nature (London)*, 173, 541 (1954).

(30) C. C. Price and H. Morita, *J. Amer. Chem. Soc.*, 75, 3685 (1953).

(31) C. D. Wagner, R. H. Smith, and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, 19, 979 (1947).

was used for the ^{13}C and ^{2}D spectra; these were recorded after carefully eliminating drift.

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Calculation of Chemical Shifts of Inner-Shell Electrons for the DNA Bases by the CNDO/2 Method Including the Charge Redistribution Effect

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Abstract: A simple treatment for the calculation of the chemical shift including the charge redistribution effect was developed by using the CNDO/2 molecular orbital method. This formalism was applied to the chemical shifts of the carbon and the nitrogen atoms in the DNA base components. For the carbon atoms, the chemical shifts were found to correlate excellently with the calculated binding energies which were obtained by the CNDO/2 method without modification of the parameters included in the method. The net charges on the carbon atoms also correspond fairly well with their chemical shifts. For the nitrogen atoms, the change of the parameters which corresponds to take the change of the core potential into account leads to a good agreement between the calculated and the observed chemical shifts. These situations were rationalized from the charge distributions of the molecules before and after the ionization of an inner-shell electron.

The finding of the chemical shift in the binding energy of the inner-shell electron has made it possible to use this method, called ESCA,[1,2] as a powerful tool for the analysis of the molecular structure of organic as well as inorganic molecules. The chemical shifts thus measured have been found to correlate intimately with the charge distribution of valence-shell electrons. Many calculations of the chemical shift have been carried out by using various molecular orbital methods, that is, the iterative extended Hückel method,[3] the CNDO method,[4] and *ab initio* calculations.[5–10] It has been shown that the charge on the atom in question could be related to its chemical shift,[3,4] but *Gelius, et al.*,[11] have indicated that the chemical shift depends not only on the charge on the ionized atom but also on the charge on the other atoms. Further, Kato, *et al.*,[12] have derived the dependency of the chemical shift on the charges of many atoms, by taking the localizing character of the inner-shell electrons into account. They applied their formalism to carbon and nitrogen atoms of many organic as well as inorganic molecules using the charges evaluated by the CNDO/2 method. A similar but somewhat different treatment has also been proposed by Ellison and Larcom.[13] In addition to this, the recent studies indicated that the charge redistribution occurs upon the ionization of an inner-shell electron and the contribution of the redistribution to the chemical shift was found not to be negligible.[12,14–16] In these researches relatively simple molecules were treated since the *ab initio* calculation for large molecules in ionized states is tremendous.

In the present paper, a relatively simple treatment of the chemical shift is developed by using the CNDO/2 method,[17–19] including the charge redistribution effect. That is, when the inner-shell electron on an atom was ionized, the valence electron is considered to feel the core potential different from that in the neutral molecule. Since all the valence electrons occupy the closed-shell orbitals before and after ionization and the chemical shift is primarily due to valence-shell electrons, the total energies of both neutral and ionized molecules can be calculated by the usual semiempirical closed-shell SCF method, that is, the CNDO/2 method. The only difference in the treatment between neutral and ionized molecules is the usage of different values for the parameters in the CNDO/2 method, which reflect the change of the core potential caused by the ionization. The treatment, details of which will be given in the following chapter, was applied to the chemical shifts of

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