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(49) It (or a very similar radical) is even formed by very prolonged photolysis of Me_3SiH in $Me_3COOCMe_3$.
(50) See, e.g., H. Fischer in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 19.
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Carbon-13 Fourier Transform CIDNP. Kinetics and Mechanism of the Photochemical Decomposition of Benzoyl Peroxide in Chloroform[1]

C. F. Poranski, Jr.,* W. B. Moniz, and S. A. Sojka[2]

Contribution from the Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375.

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Abstract: Pulsed Fourier transform NMR was used to study ^{13}C CIDNP arising from the photolysis of benzoyl peroxide in chloroform. The most intense ^{13}C CIDNP signals were those of benzene (emission) and of the phenoxy carbon of phenyl benzoate (enhanced absorption). Weak CIDNP signals were observed from CO_2 and hexachloroethane. CKO radical-pair theory was applied to explain the signs of the polarizations and provide mechanistic insight. Analysis of the time dependence of the CIDNP signals to yield rate constants and enhancement factors required incorporation of the effects of the pulse technique into the CIDNP kinetic expressions. Good agreement was obtained between rate constants derived from CIDNP data and those from chemical analysis.

The phenomenon of chemically induced dynamic nuclear polarization (CIDNP) has great potential for the mechanistic and kinetic elucidation of liquid phase radical reactions.[3] A majority of the CIDNP work has centered around the use of proton NMR spectroscopy although ^{13}C NMR offers several distinct advantages. For example, since the ^{13}C chemical shift range is quite large and since carbon nuclei are very sensitive to substituent and subtle conformational effects, it is often possible to unambiguously identify individual ^{13}C signals without the complication of overlapping lines as usually occurs in proton spectra. In addition, the spectrum can be simplified by eliminating carbon–hydrogen spin–spin splitting through the use of proton noise decoupling. Polarizations of carbons which do not bear protons can, of course, be studied directly. Finally, the utilization of pulse Fourier transform (FT) NMR methods enables the entire spectrum to be recorded in a matter of seconds, a highly desirable feature in studying the time dependence of polarized NMR signals. Carbon-13 FT CIDNP does not suffer from the disadvantage of proton FT CIDNP in which line intensities depend on the pulse flip angle because of homonuclear spin–spin couplings.[4] To judge the practicality of ^{13}C FT CIDNP as a tool for in situ material degradation studies, we have embarked on an examination of polarized ^{13}C nuclei produced during photolytic and thermal decomposition of organic compounds.

This report concerns the use of ^{13}C FT CIDNP and analytical techniques to study the photolytic decomposition of benzoyl peroxide (BPO) in chloroform. The mechanistic and kinetic conclusions obtained from the CIDNP data are compared with those obtained from product analyses. The CIDNP kinetic analysis scheme for the pulsed NMR experiment is presented for the case of a 90° flip angle, which was used in this study; the generalized treatment will appear elsewhere.[5] The thermal chemistry of BPO has been extensively studied[6] but its photochemistry has received relatively little attention.[7] CIDNP during the thermal reaction has been examined by proton[8] and $^{13}C^{9a,b}$ CW NMR and ^{13}C FT NMR.[9c]

Results

A typical ^{13}C FT CIDNP spectrum obtained during the photolysis of 0.82 *M* BPO in chloroform is shown in Figure 1. Although the CIDNP signal enhancements are large, it

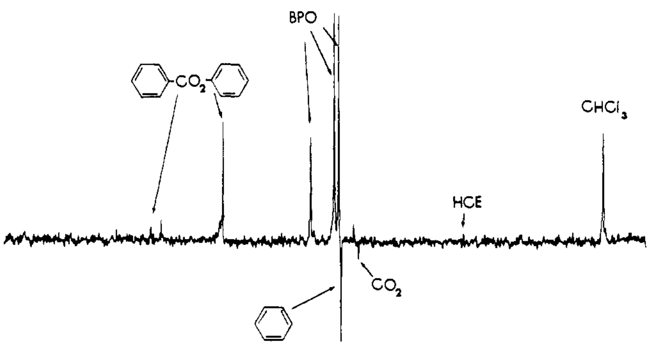


Figure 1. ^{13}C spectrum of BPO during photolysis, obtained by accumulating 64 FID's at a 10 sec pulse repetition time. Spectral width 250 ppm. Detailed assignments in Table I.

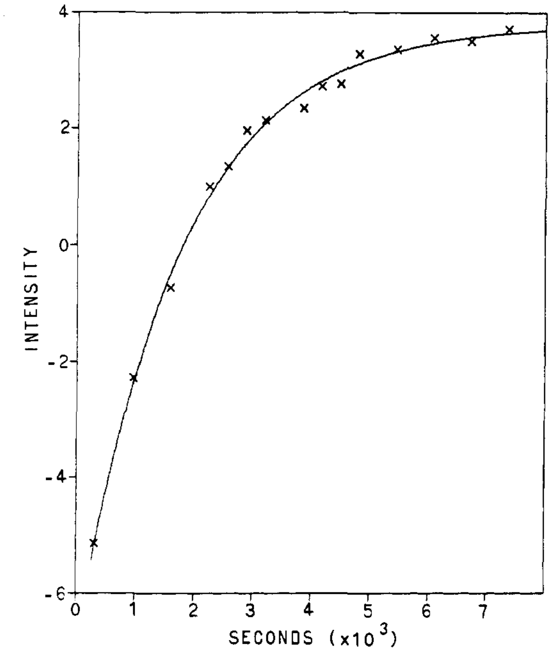


Figure 2. Integrated normalized intensity of the benzene signal vs. photolysis time: (X) experimental data; (—) computer fit to data.

was necessary to signal average over intervals of the reaction time to obtain spectra with acceptable signal-to-noise ratios. The chemical shift assignments of polarized signals were made by comparison with the chemical shifts of authentic products and by examination of the carbon-hydrogen splitting patterns in coupled spectra (Table I). Enhanced absorption was observed for α-C and C-1' of phenyl benzoate. A much weaker CIDNP absorption occurs for hexachloroethane. Emission signals were found for benzene and CO_2. The signals of BPO and chloroform were unaffected. Interestingly, the signs of the CIDNP peaks for phenyl benzoate, benzene, and CO_2 are the same as those obtained from the thermal decomposition of BPO in cyclohexanone[9b] and tetrachloroethylene.[9a] The previously reported[9] enhanced signal from C-1 of biphenyl was not found under the photolysis reaction conditions.

The areas of the polarized signals from benzene and C-1' of phenyl benzoate, normalized to the area of the chloroform signal, are plotted against photolysis time in Figures 2 and 3, respectively. The constancy of the integrated intensities of the chloroform signals indicated that no significant amount of polarized chloroform was produced during the photolysis. Each point on the plots is the accumulation of signal intensity over an interval of the reaction time and represents the experimental CIDNP curve at a time midway through the interval.[5]

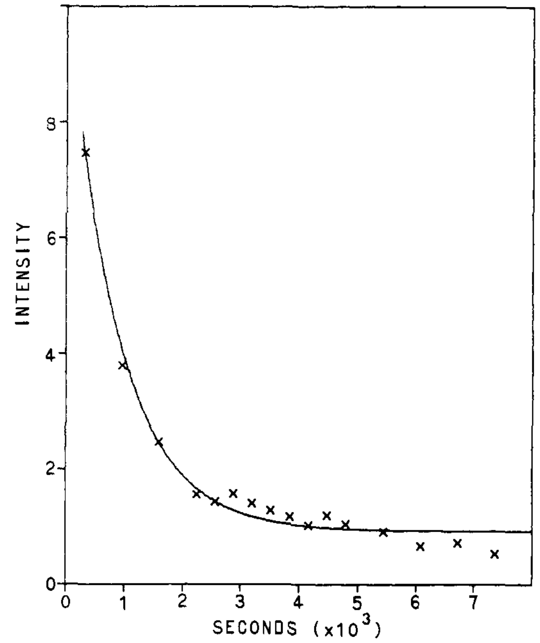


Figure 3. Integrated normalized intensity of the C-1' signal of phenyl benzoate vs. photolysis time: (X) experimental data; (—) computer fit to data.

Table I. Carbon-13 Chemical Shifts[a]

		$\delta_{^{13}C}$ (TMS)	
Compd	Carbon position	During[b] photolysis	Authentic[c] product
BPO	α	162.7	162.7
	1	133.9	133.9
	2	129.5	129.5
	3	128.6	128.6
	4	125.5	125.5
C_2Cl_6	1	107.2 (A)	106.8
CO_2	1	124.7 (E)	124.9[d]
PhH	1	128.1 (E)	128.1
PhCl	1		134.1
	2		128.4
	3		129.5
	4		126.2
PhPh	1		140.9
	2,3		128.5
	4		126.8
$PhCO_2H$	α		172.2
	1		129.2
	2		130.0
	3		128.2
	4		133.5
$PhCO_2Ph$[e]	α	164.7 (A)	164.6
	1,1'	150.9 (A)	129.7, 150.6
	2,2'		129.0, 121.4
	3,3'		128.1, 129.7
	4,4'		133.1, 125.4
$PhCCl_3$	α		97.6
	1		143.9
	2		125.2
	3		128.1
	4		130.0

[a] Chemical shifts converted to TMS scale using: $\delta_{TMS} = \delta_{CHCl_3} + 77.1$. [b] A = enhanced absorption; E = emission. [c] 25% solutions in $CHCl_3$. [d] Value reported in ref 9a and converted using $\delta_{PhH} = 128.1$. [e] Chemical shift assignments based on those in ref 9a.

Immediately after irradiation was stopped, the ^{13}C spectra of reaction mixtures were obtained under identical experimental conditions. Benzene was the only product detectable using the same number of spectral accumulations. Signals from unpolarized phenyl benzoate could be seen only after signal accumulating for approximately 30 times

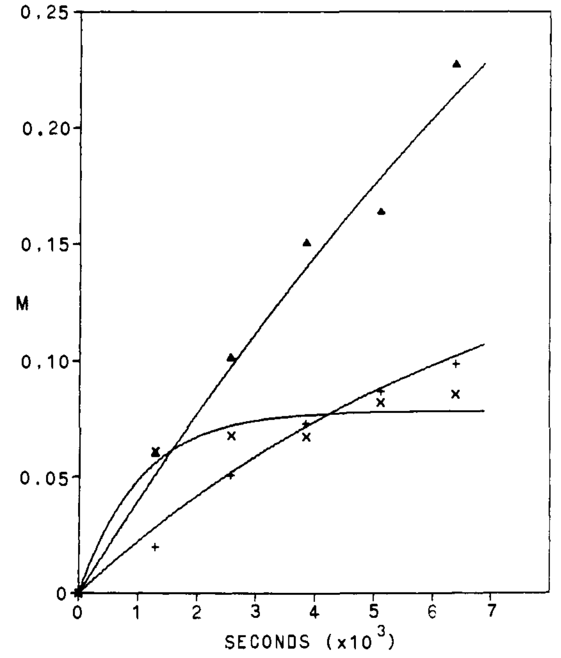


Figure 4. Photolysis product concentration vs. time: +, benzoic acid; ×, phenyl benzoate; ▲, benzene. The lines are computer fits to the experimental data.

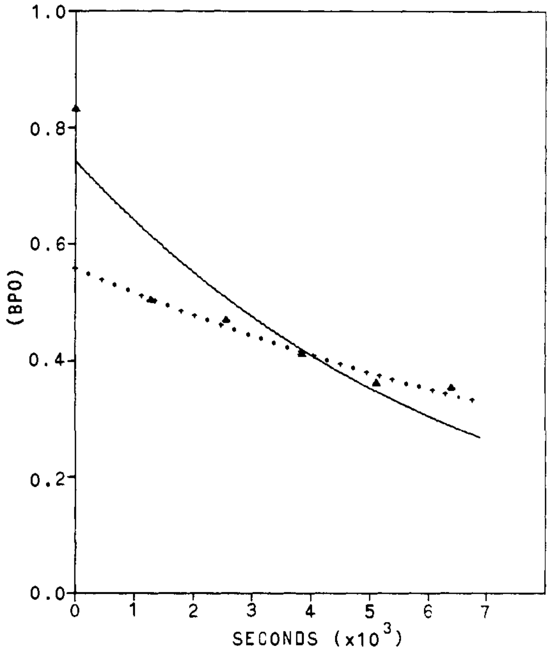


Figure 5. Benzoyl peroxide concentration vs. photolysis time (▲). The lines are computer fits to the experimental data: (—) all data points; (+ + +) initial concentration omitted (see Discussion).

Table II. Product Distribution from Photolysis of 0.83 *M* BPO in Chloroform

	Yield[a]	
Product	First period[b]	Subsequent periods[c]
PhH	1.0	6.8
PhPh	0.16	0.08
$PhCO_2H$	0.3	3.2
$PhCO_2Ph$	1.0	1.0
$PhCCl_3$	0.05	0.2
PhCl	<0.01	<0.01
C_2Cl_4	<0.01	<0.01
C_2Cl_5H	<0.01	<0.01
C_2Cl_6[d]	0.7	2.9

[a] Normalized to the yield of phenyl benzoate. [b] 0–1300 sec. [c] 1300–6400 sec. [d] Irradiation of $CHCl_3$ produced no detectable C_2Cl_6.

longer. Other reaction products could not be detected after even longer time averaging.

Combined gas chromatography-mass spectrometry (GC-MS) was used to identify and determine the amount of volatile products formed at various photolysis times. Benzoic acid was determined by base titration, and unreacted BPO was analyzed iodometrically. The material balance was approximately 80%. Table II summarizes the results of the product analyses. The time evolution of products is shown in the kinetic plots of Figures 4 and 5.

Discussion

A. Reaction Mechanisms. Reasonable reaction pathways for the photolytic decomposition of BPO in chloroform are given by eq 1-13. A number of minor pathways have not been included because of their relative unimportance as determined by product analysis. Photoexcited BPO (eq 1) undergoes peroxy bond cleavage (eq 2) to form two caged benzoyloxy radicals. Subsequent extrusion of CO_2 (eq 3) produces the benzoyloxy-phenyl radical pair, collapse of which gives phenyl benzoate (eq 4). Alternatively, escape of the radicals from the initial cage leads to products derived from solvent abstraction (eq 7-9). A second loss of CO_2 (eq 5) results in two caged phenyl radicals whose collapse gives biphenyl (eq 6). Escaped benzoyloxy radicals may undergo decarboxylation (eq 10) to produce additional phenyl radicals. Finally, other coupling reactions may occur, as shown in eq 11-13.

$$(PhCO_2)_2 \overset{h\nu}{\rightleftharpoons} (PhCO_2)_2^* \qquad (1)$$

$$(PhCO_2)_2^* \rightleftharpoons \overline{2PhCO_2\cdot} \qquad (2)$$

$$\overline{2PhCO_2\cdot} \longrightarrow \overline{PhCO_2\cdot CO_2\cdot Ph} \qquad (3)$$

$$\overline{PhCO_2\cdot \cdot Ph} \longrightarrow PhCO_2Ph \qquad (4)$$

$$\overline{PhCO_2\cdot \cdot Ph} \longrightarrow \overline{Ph\cdot CO_2\cdot Ph} \qquad (5)$$

$$\overline{Ph\cdot \cdot Ph} \longrightarrow PhPh \qquad (6)$$

$$Ph\cdot + CHCl_3 \longrightarrow PhH + \cdot CCl_3 \qquad (7)$$

$$Ph\cdot + CHCl_3 \longrightarrow PhCl + \cdot CHCl_2 \qquad (8)$$

$$PhCO_2\cdot + CHCl_3 \longrightarrow PhCO_2H + \cdot CCl_3 \qquad (9)$$

$$PhCO_2\cdot \longrightarrow Ph\cdot + CO_2 \qquad (10)$$

$$2CCl_3\cdot \longrightarrow C_2Cl_6 \qquad (11)$$

$$2Ph\cdot \longrightarrow PhPh \qquad (12)$$

$$Ph\cdot \cdot CCl_3 \longrightarrow PhCCl_3 \qquad (13)$$

B. Application of CKO Theory. In cases where a polarized product is formed by different routes, analysis of the CIDNP spectrum may determine the dominant pathway. The generally accepted Closs, Kaptein, and Oosterhoff (CKO) theory[10,11] of CIDNP can be used to explain the CIDNP results and provide some measure of mechanistic discrimination.

The sign of the net polarization is calculated by Kaptein's expression[12]

$$\Gamma = \mu\epsilon\Delta g A \qquad (14)$$

where μ refers to the multiplicity of the radical pair at the time of its formation (+for triplet pairs and pairs formed from free radical encounters, − for singlet pairs); ϵ is evaluated from the type of product-forming reaction (+ for products formed from cage collapse or disproportionation of spin

Table III. Calculated and Observed Polarizations

Product	Carbon	Radical formation Eq	μ	Product formation Eq	ϵ	Δg	A	Polarization[a] Calcd	Polarization[a] Obsd
PhH	1	3	–	7	–	–	+	E	E
	1	5, 10	–	7	–	+	–	E	
$PhCO_2Ph$	α	3	–	4	+	+	–	A	A
	1	3	–	4	+	+	–	A	N
	1′	3	–	4	+	–	+	A	A
CO_2	1	5	–	5	+	+	–	A	E
	1	10	–	10	–	+	–	E	
PhPh	1	3, 5	–	6	+	+, –	–, +	A,A	N
		3, 5	–	12	–	+, –	–, +	E,E	
$PhCO_2H$	α	3	–	9	–	+	–	E	N
	1	3	–	9	–	+	–	E	N

[a] A = enhanced absorption; E = emission; N = not observed.

sorted pairs, – for products derived from radicals which have escaped the polarizing cage); Δg is the sign of the spectroscopic splitting factor difference (+ for the radical with the larger g factor, – for the radical with the smaller g factor); A is the sign of the electron-nuclear hyperfine interaction constant. Both A factors and g values can be obtained from ESR spectroscopy and, in the case of the former, from calculations.[13] The product of these four terms determines the sense of the polarization. Γ is positive for enhanced absorption and negative for emission. Comparison of calculated and experimental polarization signs enables the predominant polarization pathway to be distinguished. Table III summarizes the net polarization predictions made by eq 14 for the various reactions.

Photoexcited BPO suffers peroxy bond homolysis to form caged benzoyloxy radicals (eq 2). Collapse of this cage to starting material has been shown by ^{18}O labeling to be minimal (~5%) for the thermal reaction.[14] The benzoyloxy radicals generated by this step cannot give rise to net polarization because the radical pair is symmetrical ($\Delta g = 0$). Therefore, barring any sorting encounters with different radical species, the products derived from these radicals will not be polarized.

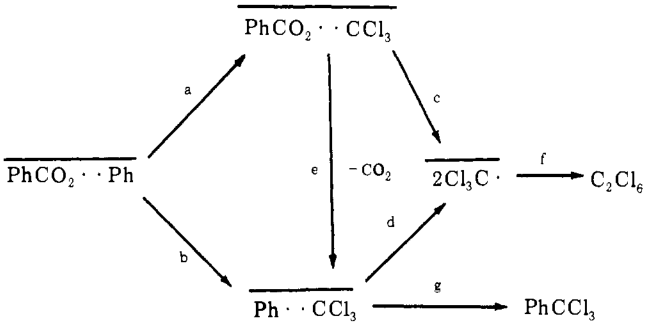
Subsequent loss of a CO_2 molecule (eq 3) generates the benzoyloxy-phenyl radical pair which can undergo spin selection. All the observed CIDNP effects can be traced back to this geminate pair. Collapse of the benzoyloxy-phenyl pair (eq 4) produces polarized phenyl benzoate. If the product precursor is a radical pair in the singlet state, agreement between the calculated and experimental sign of the net polarization is achieved with the accepted provisions that $g(PhCO_2\cdot) > g(Ph\cdot)$,[15] $A_{^{13}C}(Ph\cdot)$ is positive,[13] and $A_{^{13}C}(PhCO_2\cdot)$ is negative.[3a,16] Thus, α-C, C-1, and C-1′ are predicted to be in enhanced absorption. Unfortunately, the C-1 signal is not observable because it is obscured by BPO resonances.

The emission signal of benzene, a product resulting by abstraction of a proton from solvent by escaped phenyl radicals (eq 7), results from spin selection in the singlet benzoyloxy-phenyl radical pair. Any polarized benzene due to phenyl radicals produced by decarboxylation of escaped but sorted benzoyloxy radicals (eq 10) will be of the same sign and thus cannot be mechanistically distinguished. Likewise, escaped phenyl radicals coming from the phenyl-phenyl radical pair (eq 5) will give rise to benzene in emission. The predicted emission for another escape product, chlorobenzene (eq 8), was not detected, possibly because of the small amount of chlorobenzene produced.

A definite mechanistic choice can be made concerning the origin of the emission signal of CO_2. The CO_2 generated via eq 3 cannot be polarized because, as mentioned earlier, $\Delta g = 0$ for the benzoyloxy radical pair. Synchronous extrusion of CO_2 from BPO also would not give rise to polarized CO_2 because there is not enough time for spin states to evolve.[17] Enhanced absorption would result if CO_2 was formed directly in the spin-sorted benzoyloxy-phenyl cage (eq 5). This leads to the conclusion that the emission observed for CO_2 can only occur by the predominance of the pathway represented in eq 10, in which a benzoyloxy radical escapes the benzoyloxy-phenyl sorting cage and subsequently decarboxylates. The relatively long lifetime of the benzoyloxy radical[6b,18-20] is consistent with this interpretation of the CIDNP results.

The production of polarized hexachloroethane appears to be an example of Kaptein's "memory effect"[11a,c] or Cooper, Lawler, and Ward's "pair substitution".[19] In this rationale (Scheme I) one of the partners of the geminate benzoyloxy-phenyl radical pair abstracts a hydrogen atom from chloroform (pathways a and b), and is replaced in the cage by the resulting trichloromethyl radical.[21] A second substitution is required in which the remaining partner of the original geminate pair reacts and is replaced by another trichloromethyl radical (pathways c and d). The benzoyloxy-trichloromethyl radical pair may lose CO_2 to give the phenyl-trichloromethyl radical pair (pathway e), but this cannot be an important process as the CO_2 would be in enhanced absorption (emission is observed, see Table III). The spin multiplicity of the new trichloromethyl-trichloromethyl pair is the same as that of the original benzoyloxy-phenyl pair since the substitution reactions are rapid and spin is conserved. Hence, enhanced absorption is predicted for hexachloroethane (pathway f). A reasonable alternative mechanism for formation of polarized hexachloroethane is not apparent at this time. Collapse of the phenyl-trichloromethyl pair produced via pathways a and e or b is predicted to yield enhanced absorption for both C-1 and α-C of α,α,α-trichlorotoluene (pathway g); however, no polarization was observed for this product.

Scheme I



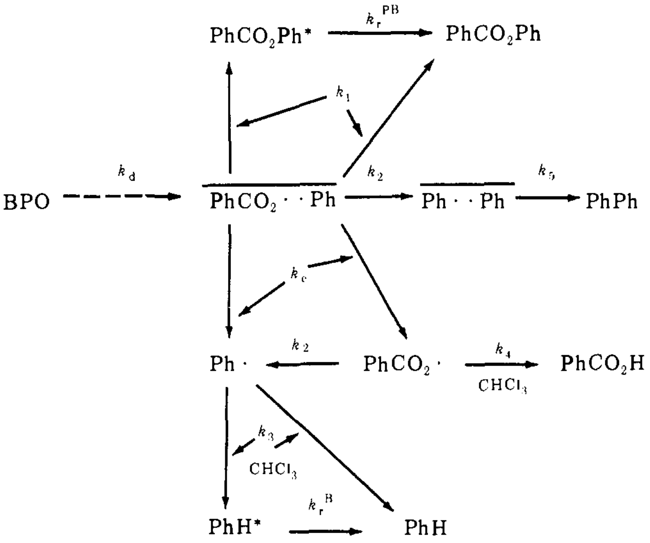
Although it is a product in both the thermal and photochemical reactions, biphenyl was polarized only in the thermal reaction (enhanced absorption).[9] This polarization is an example of cage collapse (eq 5 and 6) since emission would result for diffusive encounters of free but sorted phenyl radicals (eq 12). As the temperature of the thermal decomposition was lowered the intensity of the polarized signal of biphenyl was severely reduced.[9b] This is consistent with the observation that the yield of CO_2 increases with temperature.[22] It appears likely from these data that the second extrusion of CO_2 from the benzoyloxy-phenyl geminate pair (eq 5) cannot compete effectively with diffusion processes. A longer lifetime of the benzoyloxy radical at the lower temperature of the photochemical reaction could account for the lack of biphenyl CIDNP.

Polarization has not been observed from benzoic acid in either the thermal or photochemical reactions. Emission is predicted from the carbonyl carbon of benzoic acid produced via eq 9 in which a presorted benzoyloxy radical escapes the polarizing cage. It is not likely that the polarization is lost by electron-nuclear relaxation due to the longevity of the benzoyloxy radical, since polarized CO_2 results from this same species.

All of the observed polarization signs are consistent with a singlet radical pair precursor. Since the multiplicity is conserved in the act of bond rupture (eq 2 and 3), direct photoexcitation (eq 1) produces BPO mainly in the singlet excited state. Other photolyses studies have shown that direct irradiation of BPO does indeed generate singlet states.[23] In order to verify this conclusion the photolysis was performed using acetophenone as triplet sensitizer[7h,23] and, as predicted by theory, the signs of the polarizations for phenyl benzoate and benzene were opposite to those observed under direct irradiation, by virtue of the triplet multiplicity of the benzoyloxy-phenyl radical pair.

C. Kinetics of BPO Photolysis. As the purpose of this work was not only to apply FT NMR to mechanistic but also to kinetic studies of CIDNP reactions, parallel chemical and CIDNP kinetic analyses were made. The general model used for both approaches is shown in Scheme II. The radical pair, $\overline{PhCO_2\cdot\ \cdot Ph}$, reacts by cage collapse processes (rate constant $k_c = k_1 + k_2$) and by diffusion controlled escape (rate constant k_e). Alternative reaction paths are shown for benzene and phenyl benzoate to differentiate between the chemical and CIDNP kinetic schemes. The chemical kinetic scheme will be considered first, followed by the CIDNP scheme. The experimental results will then be compared and discussed in the context of the predictions of Scheme II.

Scheme II



Chemical Kinetics. Using the steady state approximation for the cage pair and the intermediate radicals and assuming that BPO disappears by first-order kinetics, the following expressions are obtained for the chemical kinetic analysis of the major products:

phenyl benzoate

$$[\mathrm{PB}] = \frac{k_1}{k_c + k_e}[\mathrm{BPO}]_0(1 - e^{-k_d t}) \qquad (15)$$

benzoic acid

$$[\mathrm{BA}] = \frac{k_4 k_e}{(k_c + k_e)(k_2 + k_4)}[\mathrm{BPO}]_0(1 - e^{-k_d t}) \qquad (16)$$

benzene

$$[\mathrm{B}] = \frac{k_e}{k_c + k_e}\left[1 + \frac{k_2}{k_2 + k_4}\right][\mathrm{BPO}]_0(1 - e^{-k_d t}) \qquad (17)$$

The total rate constant for cage collapse, k_c, is effectively equal to k_1 (10^{10} sec^{-1}),[6b] since k_2, the rate constant for benzoyloxy radical decarboxylation, is negligibly small by comparison to k_1 (3.3×10^3 sec^{-1} at 44°[24] to $\sim 10^7$ sec^{-1}[20]). Cage escape is a diffusion limited process, and $k_e \simeq k_{\mathrm{diff}}[\mathrm{CHCl_3}] = 1.2 \times 10^{11}$ sec^{-1}.[25] The pseudo-first-order rate constants, k_3 and k_4, for phenyl radical and benzoyloxy radical proton abstraction from the chloroform solvent are calculated[26] to be 3.7×10^7 and 1.5×10^7 sec^{-1}, respectively.

Using the above values for the various rate constants, eq 15-17 may be evaluated to give an estimate of the product yields. Thus, for the cage collapse pathway, eq 15 becomes

$$[\mathrm{PB}] = 0.077[\mathrm{BPO}]_0(1 - e^{-k_d t}) \qquad (18)$$

In the case of cage escape products the relative amounts of benzene and benzoic acid predicted by eq 16 and 17 will vary considerably depending on the value chosen for k_2, since here k_2 may or may not be negligible with respect to k_4. If the lower value, $k_2 = 3.3 \times 10^3$ sec^{-1}, is used, k_2 is negligible with respect to k_4 and both eq 16 and 17 reduce to eq 19a which predicts a 1:1 ratio of benzene to benzoic acid.

$$[\mathrm{B}] = [\mathrm{BA}] = 0.923[\mathrm{BPO}]_0(1 - e^{-k_d t}) \quad (k_2 = 3.3 \times 10^3\ \mathrm{sec}^{-1}) \qquad (19a)$$

If a higher value, $k_2 = \sim 10^7$ sec^{-1}, is used, k_2 cannot be neglected and eq 16 and 17 become 19b and 19c, respectively.

$$[\mathrm{BA}] = 0.55[\mathrm{BPO}]_0(1 - e^{-k_d t}) \qquad (19b)$$

$$[\mathrm{B}] = 1.3[\mathrm{BPO}]_0(1 - e^{-k_d t}) \quad (k_2 = 10^7\ \mathrm{sec}^{-1}) \qquad (19c)$$

CIDNP Kinetics. The approach used to obtain kinetic information from CIDNP data is that developed by Walling and Lepley.[29] In the simplest case reactant R forms polarized product P* with rate constant k, and P* relaxes to product P with rate constant $k_r = 1/T_1$ (eq 20). Electron-nuclear relaxation is ignored. For this two-step consecutive first-order reaction scheme, the intensity, at any time, of an NMR line from P is described by eq 21, where I^* and I are

$$\mathrm{R} \xrightarrow{k} \mathrm{P}^* \xrightarrow{k_r} \mathrm{P} \qquad (20)$$

$$I_t = I^* + I = \alpha[\mathrm{P}^*] + \beta[\mathrm{P}] \qquad (21)$$

contributions to the line intensity from polarized and relaxed product, respectively. The coefficients, α and β, are

Table IV. Constants Obtained from Computer Fit of Product Analysis and CIDNP Data

		All data			Initial points omitted		
Method	Compd	a	b	c, 10^{-4} sec^{-1}	a	b	c, 10^{-4} sec^{-1}
Product analysis	PhH	0.601	−0.598	0.7	0.615	−0.610	0.7[b]
	$PhCO_2Ph$	0.079	−0.078	9.7	0.066	−0.066	1.2[b]
	$PhCO_2H$	0.174	−0.177	1.4	0.124	−0.148	2.7
	BPO[a]		0.742	1.5		−0.558	0.8
CIDNP	PhH	0.380	−1.070	5.7	0.374	−1.150	6.1
	$PhCO_2Ph$	0.092	0.926	11.3	0.054	0.359	4.6

[a] Fit to an equation of the form $Y = be^{-ct}$. [b] Curve-fitting program did not converge; manual iteration used.

defined as NMR extinction coefficients. Using the steady state approximation for P*, setting $[P] = [R]_0 - [R]$ and $I_\infty = \beta[R]_0$ (at the end of the reaction all R has formed relaxed P), eq 22 may be written, from which k and, if k_r is

$$\ln\left(\frac{I_t - I_\infty}{I_\infty}\right) = \ln\left[\frac{\alpha}{\beta}\cdot\frac{k}{k_r} - 1\right] - kt \qquad (22)$$

known, the enhancement factor, α/β, may be obtained. Equation 22 is useful only if an unambiguous determination of I_∞ can be made, such as by direct measurement after complete reaction. If the reaction does not go to completion, or if I_∞ is too weak to be observed, eq 22 may be written in the exponential form, eq 23, and the constant terms I_∞, k,

$$I_t = I_\infty + I_\infty\left[\frac{\alpha}{\beta}\cdot\frac{k}{k_r} - 1\right]e^{-kt} \qquad (23)$$

and $[(\alpha/\beta)\cdot(k/k_r) - 1]$ obtained by a computer fit of the data.

The above derivation is applicable to the CW NMR experiment. Analysis of the kinetic behavior of the CIDNP signals is modified by the use of pulsed NMR techniques. First, if signal averaging is employed, as is generally the case for ^{13}C FT NMR, each measurement represents not an instantaneous intensity, but a sum of intensities taken at periodic intervals during a time segment of the reaction. Second, if a 90° pulse is used,[30] as in the present work, the total net magnetization, M_z, is tipped into the x-y magnetization plane, where the free induction decay signal is measured. Since natural relaxation processes restore only a Boltzmann population along M_z, the P* which existed at the time of the pulse is permanently lost. Subsequent z magnetization due to P* occurs only with the formation of new P* and this has to be treated as a new kinetic event after each pulse, starting with a new pseudo-initial concentration of reactant. A complete derivation of pulsed CIDNP kinetics will be presented elsewhere.[5] With the modification required by the pulse accumulation technique the equation for the analysis of the CIDNP kinetics of benzene and phenyl benzoate according to Scheme II is given by eq 24 where $I_j(i)$ = signal intensity accumulated over N 90° pulses during collection period j, A_0 = initial concentration of reactant, f = fraction of reactant which forms product i, $R = (1 - e^{-k_r\tau})$, which describes restoration of M_z of product i during interval τ between pulses, Ω = a constant determined by the kinetic scheme, $(e^{-k_d\tau} - e^{-k_r\tau})$ = growth-decay of polarized i during the interval between pulses, $g(t)$ = time from start of reaction to midpoint of collection period j.[5] Equation 24 requires that the first pulse of the first collection period be applied at τ seconds after the initiation of the reaction, and that the first pulse of each successive collection period occur τ seconds after the last pulse of the preceding period.

$$I_j(i) = NA_0\beta fR + NA_0[\alpha\Omega(e^{-k_d\tau} - e^{-k_r\tau}) - \beta fR]e^{-g(t)k_d} \qquad (24)$$

Based on the CIDNP pathways of Scheme II the rate constant terms, Ω, for phenyl benzoate and benzene[31] are

$$\Omega^{PB} = \frac{k_1 k_d}{(k_c + k_e)(k_r^{PB} - k_d)} \qquad (25a)$$

$$\Omega^{B} = \frac{{}^1\!/_6 k_e k_d}{(k_c + k_e)(k_r^{B} - k_d)}\left[1 + \frac{k_2}{k_2 + k_4}\right] \qquad (25b)$$

Rate Constants Obtained from Product Analysis and CIDNP Data. In order to make meaningful comparisons of the analytical and the CIDNP results, the validity of the kinetic scheme must be established. However, both the CIDNP and product analysis data indicate the presence of anomalies during the initial portion of the reaction which affect the kinetic and mechanistic interpretations. As is detailed in the next section, the evidence readily justifies separate consideration of the well-behaved portion of the reaction. Emphasis may therefore be placed on a principal interest of this work, which is the evaluation of pulsed FT NMR as a kinetic tool in CIDNP reactions. The anomalies are discussed subsequently.

Determination of k_d. The chemical (eq 15-17) and CIDNP (eq 24) kinetic expressions are of the same general form, $Y = a + be^{-ct}$. The experimental data were fit to this expression by a curve-fitting program,[32] to obtain best values for the three constants a, b, and c. The form of eq 15-17 requires that $a = -b$ for the chemical case but such a constraint was not imposed on the computer analysis. The results of the computer fits are given in Table IV and the curves are plotted in Figures 2-5.

Constant c in Table IV is k_d (Scheme II), the effective rate constant for the rate-determining step in the decomposition of BPO which leads to the formation of the benzoyloxy-phenyl cage pair. The k_d's obtained from the product distribution analyses of the indicated compounds are self-consistent, with the exception of that for phenyl benzoate which is anomalously large. The k_d's obtained from the CIDNP data are larger than those from the product analysis data. However, the values of k_d obtained for phenyl benzoate by both methods are comparable.

Inspection of the BPO plot (Figure 5) shows that the computer-derived curve is a rather poor fit to the experimental data due to the precipitous decrease in BPO concentration during the early stages of the reaction (≈0-1300 sec). This behavior is reflected in the analytical data for phenyl benzoate (Figure 4) and biphenyl, which show rapid growth in concentration during the same time period. Other observed products are not similarly affected. The data in Table II show that the product distribution is markedly different during the first reaction period (0-1300 sec) than it is during the remainder of the reaction time (1300-6400 sec), changing from roughly a 50-50 mix of cage collapse to cage escape products initially to a 10-90 mix subsequently.

These observations, coupled with the anomalously high k_d obtained for phenyl benzoate, strongly suggest that during the early stages of the reaction, BPO may photolyze by a process which competes with that given by eq 1 and 2, and which is discussed later.

To test this hypothesis, both the chemical and the CIDNP data were subjected to curve fitting with the data points prior to 1300 sec omitted. The k_d's thus obtained are also shown in Table IV. Inspection shows that the k_d's are more self-consistent within each method for the adjusted data. Furthermore, Figure 5 illustrates that the experimental points for the BPO time dependence are nicely fit in the case of the adjusted data. The k_d's obtained from the CIDNP data remain larger than those obtained from the product analysis data but are well within an order of magnitude of them. Thus, the CIDNP and product analysis kinetic results for k_d agree within acceptable limits if the anomalous initial reaction period is excluded.

Estimation of Other Rate Constants. Using the chemical kinetic analysis data, the validity of the literature rate constants used in deriving eq 18 and 19 may be examined. In keeping with the conclusions reached in the preceding section, only the well-behaved portion of the reaction will be considered. Constant a (or b) derived from the product analysis results (Table IV, initial points omitted), when divided by the initial BPO concentration (0.558 M), yields the experimentally determined coefficients of eq 15-17, which can be compared with the values calculated using literature-based rate constants (eq 18 and 19). The experimental values of $0.5(a + b)/[\mathrm{BPO}]_0$ are 0.12, 1.10, and 0.25 for phenyl benzoate, benzene, and benzoic acid, respectively. Thus, approximately 15% cage collapse is observed, compared to the 7.7% which is expected (eq 18). The values of k_c and k_e, therefore, are in roughly the correct ratio (a doubling of k_c or a halving of k_e would raise the predicted yield of cage collapse products to 14%).

The experimentally observed ratio, benzene:benzoic acid, is 4.4 which supports the higher value of the benzoyloxy decarboxylation rate constant, $k_2 \approx 10^7\ \mathrm{sec}^{-1}$, used in evaluating the coefficients of eq 19b and 19c. The predicted ratio would be 4.3 if $k_2 = 2.5 \times 10^7\ \mathrm{sec}^{-1}$.

Virtually the same conclusion concerning the magnitude of k_2 can be reached in the case of biphenyl. The observed yield of biphenyl (Table II) is several orders of magnitude larger than calculated using $k_2 = 3.3 \times 10^3\ \mathrm{sec}^{-1}$, and assuming $k_5 \simeq k_1$. Barring significant biphenyl production via routes not specified in Scheme II (for example, phenyl radical encounters), a much larger decarboxylation rate constant for benzoyloxy radical is indicated.

The Initial Reaction Period. It is of interest to speculate on the kinetic anomalies which were observed during the first reaction period involving BPO, phenyl benzoate, and biphenyl. Any rationale must take into account that these are the only analyzed compounds affected and that, for the same time period, the CIDNP intensity from phenyl benzoate appears to be augmented. Contributions from zero- and second-order kinetics might be expected in view of the concentrated solutions used in this study. The most likely second-order process, induced decomposition, would yield primarily substituted benzoic acids and increase the concentration of benzoyloxy radicals.[33] Since the benzoic acid and benzene first-order plots are well behaved, induced decomposition cannot be of major importance. Furthermore, polarized phenyl benzoate would not be produced by this process. On the other hand, while a zero-order reaction would yield polarized phenyl benzoate, it would also lead to accelerated formation of all the products.

An alternative explanation is multiple bond cleavage of photoexcited BPO, whereby CO_2 (unpolarized) and the benzoyloxy-phenyl radical pair are formed in a single step. This mechanism is appealing since it satisfies all the observations with the reasonable assumption that the benzoyloxy-phenyl radical pair produced by this process has a higher probability of collapse because of the closer initial proximity of the radicals in the cage. Spin sorting commences immediately, unlike the situation considered earlier (eq 1-3), where decarboxylation of one of the two benzoyloxy radicals must first occur.

Spin sorting cannot occur if the multiple bond cleavage step is a concerted process in which the benzoyloxy and phenyl radicals collapse to phenyl benzoate synchronously with the extrusion of CO_2. However, there is both product evidence and CIDNP evidence that synchronous collapse/extrusion does not occur exclusively: (1) the relative yield of biphenyl as well as of phenyl benzoate is increased during the first period, indicating that time for decarboxylation of benzoyloxy radical exists; and (2) the CIDNP intensity of phenyl benzoate is strongly augmented during the same period, indicating sufficient lifetime for phenyl/benzoyloxy spin sorting. The signs of the product polarization for this radical pair formed in a one-step process are of course identical with those determined for its formation via the stepwise process of eq 1-3.

It is not immediately apparent why the additional initial process ceases to contribute. It is plausible that the postulated multiple bond cleavage process becomes less important upon the destruction of an undetermined sensitizer, or upon buildup of reaction products which may act as filters or quenchers.

Calculation of Enhancement Factors. The CIDNP enhancement factors, α/β, for benzene and phenyl benzoate can be obtained by calculating the values of α and β from the computer derived CIDNP b's and a's (Table IV) and eq 24: $a = NA_0\beta fR$; $b = NA_0[\alpha\Omega(e^{-k_d\tau} - e^{-k_r\tau}) - \beta fR]$. For the well-behaved region from ~1300 sec on, $A_0 = 0.558\ M$. The relaxation rates, $k_r\ (= 1/T_1)$, for benzene and the C_1' carbon of phenyl benzoate were obtained from the measured T_1's of 34 and 47 sec, respectively. The average of the two k_d's obtained for the CIDNP data (Table IV) is $5.3 \times 10^{-4}\ \mathrm{sec}^{-1}$. In this work, $N = 64$. The term f is defined as the fraction of reactant forming a given product and is 0.12 for phenyl benzoate and 1.1 for benzene. Then, from eq 25, $\Omega^{PB} = f^{PB}[k_d/(k_r^{PB} - k_d)]$ and $\Omega^{B} = f^{B}(1/6)[k_d/(k_r^{B} - k_d)]$. The resulting enhancement factors are 300 for phenyl benzoate and −690 for benzene.

Conclusions. This study of ^{13}C CIDNP in the photochemical decomposition of benzoyl peroxide in $CHCl_3$ has demonstrated that pulsed FT NMR techniques can be successfully applied to obtain both mechanistic and kinetic information about reactions which display the CIDNP phenomenon. Interpretation of the signs of the polarized ^{13}C signals provides mechanistic insight on the reaction pathways. The accumulation of signals, necessary in ^{13}C FT work, provides no serious obstacle to CIDNP data kinetic analysis when a 90° pulse angle is used. There is good agreement between the results obtained by kinetic analyses of the CIDNP and chemical data. Both the CIDNP and chemical results for phenyl benzoate revealed the existence, in the early part of the reaction, of a process involving additional cage collapse, quite possibly multiple bond cleavage, leading to faster initial rates of formation of phenyl benzoate and biphenyl and accelerated consumption of benzoyl peroxide. In the "well-behaved" region, the chemical data fit a kinetic model, Scheme II, if the rate of decarboxylation of benzoyloxy radical is $\sim 10^7\ \mathrm{sec}^{-1}$.

Experimental Section

Chemicals. BPO from K&K Laboratories, Inc. was twice dissolved in chloroform and reprecipitated by addition of methanol. The collected crystals were dried under vacuum and analyzed iodometrically to be 97.5% pure. Reagent grade chloroform was washed three times with water, dried over anhydrous Na_2SO_4, distilled, and deaerated by a stream of high purity nitrogen.

Photolysis Experiments. The broad band radiation from a 600 W mercury-xenon arc source was focused through a water filter and Corning glass filters number CS-954 and CS-054 and onto the flat, polished end of a 7 mm diameter quartz rod. The quartz rod served as a light pipe to bring the radiation through a large 90° arc and into the bottom of the 8 mm probe insert and terminated 1 mm from the end of the NMR sample tube. The BPO samples had an absorbance of 1 (5 mm path length) at 320 nm. The Corning filters had a combined transmittance of greater than 50% at wavelengths longer than 315 nm, and less than 1% at wavelengths shorter than 305 nm. The use of the filters eliminated detectable photodecomposition of chloroform itself without adversely affecting the CIDNP intensities.

Carbon-13 NMR Measurements. Proton decoupled natural abundance carbon-13 spectra were measured at 25.15 MHz with a Varian HA-100 spectrometer modified for pulsed Fourier transform operation and equipped with an external F-19 field-frequency lock.[34] Signals were accumulated in a Nicolet 1074 signal averager and Fourier transformed by a PDP-8/L computer. Identical phase corrections were applied to spectra obtained before, during, and after irradiation. CIDNP spectra were accumulated during intervals of the reaction on aliquots of 0.8 M BPO in chloroform. Each interval consisted of 64 spectral collections with a pulse repetition time of 10 sec. Four CIDNP runs were made. For each run, data were collected in 1K blocks during four reaction intervals. Collection periods were staggered so that most data points interleaved; good agreement was obtained among samples. Benzene was the only product to give a detectable signal in the dark spectra after 64 accumulations. Phenyl benzoate was the only other product which was detectable after an overnight run of several thousand accumulations.

Thin wall Pyrex sample tubes with 7.5 mm outside diameters were used for the photolysis experiments. The probe temperature was 44 ± 2° and a 90° pulse took 108 μsec. Carbon resonances were assigned by comparison with authentic samples run as 25% solutions in chloroform. Chemical shifts were converted to the TMS scale using: $\delta_{TMS} = \delta_{CHCl_3} + 77.1$. When necessary for assignments, pulsed decoupling was used to obtain proton-coupled spectra with the NOE retained.[35] The value of T_1 for C-1′ of phenyl benzoate (47 sec) was determined on a saturated chloroform solution into which CO_2 had been bubbled. The T_1 for benzene (34 sec) was determined on a 70% solution in chloroform saturated with CO_2. The progressive saturation technique[36] was used for T_1 measurements and the data were fit to the equation $I = I_\infty(1 - e^{-\tau/T_1})$ by a computer program[37] in which both T_1 and I_∞ were optimized.

Product Analysis. A Hewlett-Packard Model 5700A/5930A GC-MS system was used to identify the products of the photolysis reaction. Since BPO decomposes at about 110°, interfering with the determination of the higher boiling compounds, the quantitative GC analysis consisted of two parts. First, a 0 to 200° programmed run on the 5700A was used to analyze for the lower boiling compounds up to hexachloroethane. Then the solutions were evaporated to dryness and isopentane was added to dissolve all of the residue but BPO and benzoic acid, which were removed by filtration. The solutions were again evaporated to dryness and the residues were redissolved in chloroform. These solutions were run on a Perkin-Elmer Model 900 GC (100-175° at 16°/min) to analyze for α,α,α-trichlorotoluene, biphenyl, and phenyl benzoate. The internal standard was 3,4-dichlorotoluene in both analyses. Triplicate GC analyses were carried out on each sample. Unreacted BPO was determined iodometrically; benzoic acid was titrated with standardized NaOH.

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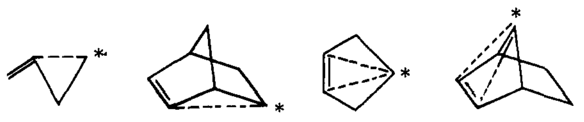
Homoallylic Interaction between the Nitrogen Lone Pair and the Nonadjacent π Bond in Cyclic and Bicyclic Amines. I. Photoelectron Spectroscopic Study[1]

Isao Morishima,[2]* Kenichi Yoshikawa, Mikio Hashimoto, and Katsutoshi Bekki

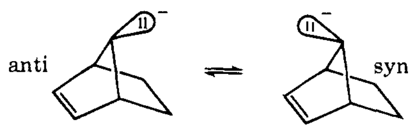
Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received September 16, 1974*

Abstract: In order to study the nonadjacent n,π electronic interaction, photoelectron spectra have been obtained for saturated and unsaturated derivatives of five- and six-membered cyclic and bicyclic amines. It was found that perturbation of nitrogen lone pair ionization potentials (IP's) induced by the interaction with nonadjacent carbon–carbon double bond is quite different in β,γ-unsaturated five-membered cyclic amines and β,γ-unsaturated six-membered amines. The bishomoallyl homoconjugation in five-membered amines favors n,π through-space interaction with destabilization of lone pair orbital, and homoallyl conjugation in six-membered amines involves n,π and n,π* interactions with a little stabilization or destabilization of the lone pair orbital. Different features of lone pair IP's were also encountered for *N*-H and *N*-methyl derivatives of six-membered amines. These were discussed in terms of relative importance of n,π and n,π* interactions which depend on molecular symmetry (bishomoallyl or homoallyl interaction), orbital energy level, and orientation of lone pair in cyclic and bicyclic amines.

During the last decade, the consequences of homoconjugation between an unsaturated group and an active center in cations, radicals and anions have been a subject of controversy. Particularly, studies on the interaction between the cation center and the nonadjacent π bond have been extensively performed[3] in connection with the debate on "the nonclassical carbonium ion". The great π electron participation in the acceleration of the rate of solvolysis in norbornene derivatives has been well established. Concerning the interaction between the half-occupied orbital and the nonadjacent π bond, Kochi et al.[4] have reported the ESR studies of 7-norbornenyl radical, and claimed that the configuration with the sp hybrid orbital directed toward the anti side is the most stable form, and that the interaction between the orbitals of carbon 2,3 and the half-occupied orbital on carbon 7 would have a destabilizing effect.

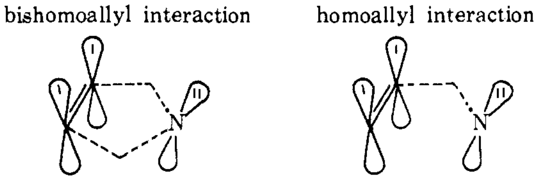

* = cation, radical, anion

However, the studies on the nonbonded interaction between the doubly occupied n orbital (anion center) and the nonadjacent π group have been quite limited. Recently Stille et al.[5] have speculated, based on the experimental results of the 7-norbornenyl anion system, that bishomoallyl type interaction makes the n-π interacting system less stable due to the antiaromatic character. The conformation of 7-norbornenyl anion has also been examined quantum chemically using CNDO/2 and MINDO/2 MO calculations by Santry[6] and Dewar,[7] respectively. However, these semiempirical MO calculations failed to predict definitely the orientation of lone pair electrons affected by the neighboring double bond in the 7-norbornenyl anion.[8] Consequently, the interaction between the lone pair electrons and the nonadjacent π electrons (homoallyl type interaction) is still open to further experimental and theoretical studies.



Recently photoelectron spectroscopy (PES) has proved to be extremely useful in evaluating the electronic interaction between nonadjacent groups[9] in the ground state molecules. The usefulness of PES in studying π,π interactions in dienes and n,n interactions in various nitrogen and oxygen containing molecules has been demonstrated.[10] The PES studies concerning n,π interactions in unsaturated ketones and ethers have also been reported.[11] However, there have been no systematic studies[12] on the n,π interaction between nitrogen lone pair and nonadjacent olefin or benzene π electrons.

In order to elucidate the structural effect on the homoconjugative interaction between lone pair and π electrons, we have performed here a PES study of nonadjacent n,π interaction in various cyclic and bicyclic amines (**1–18**). Here we are concerned with difference in the intrinsic nature of homoallyl and bishomoallyl n,π interactions. Amines containing the nonadjacent unsaturated group seem to be quite relevant for the study of the intramolecular n,π interactions. The PES study on this n,π homoconjugative interac-


bishomoallyl interaction

homoallyl interaction

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