Interaction between Closed- and Open-Shell Molecules. VII. Carbon-13 Contact Shift and Molecular Orbital Studies on the Charge-Transfer Interaction between Halogenated Molecules and Nitroxide Radical[1]

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Abstract: ^{13}C nmr contact shifts induced by the addition of di-*tert*-butyl nitroxide radical (DTBN) were observed for halomethanes, haloethanes, and halobenzenes. The downfield ^{13}C contact shifts for the carbon bonded directly to halogen were more pronounced for bromide and iodide than chloride. These results were interpreted in terms of the charge-transfer (CT) interaction between the DTBN radical and halogenated molecules in the manner of C–X· · ·DTBN interaction. Approximate values of the formation constants, enthalpies, limiting ^{13}C contact shifts, and spin densities on the carbon were also determined for this CT complex formation. Theoretical studies on this interacting system were also performed by the unrestricted Hartree–Fock SCF–MO (INDO method) calculations. The stabilization energies and spin densities on the acceptor carbon were well reproduced by the MO calculation. The positive spin density on DTBN is transferred directly onto the C–X antibonding orbital of halomethane by the spin delocalization mechanism. On the basis of the present experimental and theoretical studies, the mechanism of halogen abstraction reaction was discussed briefly.

Recently we have demonstrated[3] that the nmr contact shift study provides a potential tool for the investigation of molecular interaction between free radical and various closed-shell molecules. The hydrogen bond between the nitroxide radical and various proton donor molecules induces quite sensitively upfield and downfield proton and ^{13}C contact shifts for proton donor molecules.[3a,b] It has been shown that the spin densities on the donor molecules induced by the hydrogen bond with nitroxide radical yield fruitful information on the nature of the hydrogen bond with the free radical. As a part of our continuing studies on the interaction between closed-shell and open-shell molecules, we here report ^{13}C nmr contact shift studies on nitroxide radical–alkyl halide interaction which are interpreted in terms of a charge-transfer (CT) interaction.

There has been much evidence of weak donor–acceptor complex formation between halogenated methanes and electron donor molecules from uv,[4] ir,[5] and Raman[6] spectroscopic studies and from measurements of heat of mixing.[7] However, these studies were associated with the interaction between closed-shell molecules and there have been only limited studies on the donor–acceptor interaction between closed- and open-shell molecules.[8] The study of radical-induced nmr contact shift is expected to provide direct information on this type of interaction, particularly on the mode of electron spin transfer from radical (electron donor) to halogenated molecules (electron acceptor). The use of ^{13}C nmr spectroscopy appears to be relevant to the present study because tetrahalomethane is most appropriate to this work as an electron acceptor and ^{13}C nmr shift is quite sensitive to the presence of the paramagnetic species.[3,9] It seems also quite interesting to investigate the CT interaction between free radical and halogenated molecules from the viewpoint that this interaction is considered to be associated with the transition state of the halogen abstraction reaction.

Here we used di-*tert*-butyl nitroxide (DTBN) as an electron donor free radical and halomethanes, haloethanes, halobenzenes, and some other halogenated molecules as an electron acceptor. We followed ^{13}C contact shifts induced by the addition of DTBN to the solution of halogenated molecules. The ^{19}F nmr contact shift was also measured for some fluorinated molecules.

Experimental Section

Materials. DTBN was prepared by referring to Briere and Rassat.[10] 1-Bromo-2-iodoethane was synthesized according to the method of Simpson.[11] All other chemicals used in this study were commercially available.

^{13}C **Nmr Measurement.** Completely proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a Jeolco C-60HL spectrom-

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(3) (a) I. Morishima, K. Endo, and T. Yonezawa, *J. Amer. Chem. Soc.*, **93**, 2048 (1971); (b) *Chem. Phys. Lett.*, **9**, 143 (1971); (c) *ibid.*, **9**, 203 (1971); (d) I. Morishima, T. Inubush, K. Endo, and T. Yonezawa, *ibid.*, in press.

(4) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962); R. Anderson and J. M. Prausnitz, *J. Chem. Phys.*, **39**, 1225 (1963).

(5) P. Datta and G. M. Barrow, *J. Amer. Chem. Soc.*, **87**, 3053 (1965).

(6) D. A. Bahnick and W. B. Person, *J. Chem. Phys.*, **48**, 1251 (1968).

(7) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **63**, 2063 (1966).

(8) Y. Y. Lim and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 891 (1971); Y. Murata and N. Mataga, *Bull. Chem. Soc. Jap.*, **44**, 354 (1971).

(9) I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **92**, 6651 (1970); I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971); I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972).

(10) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 273 (1965).

(11) M. Simpson, *Ber.*, 7, 130 (1874).

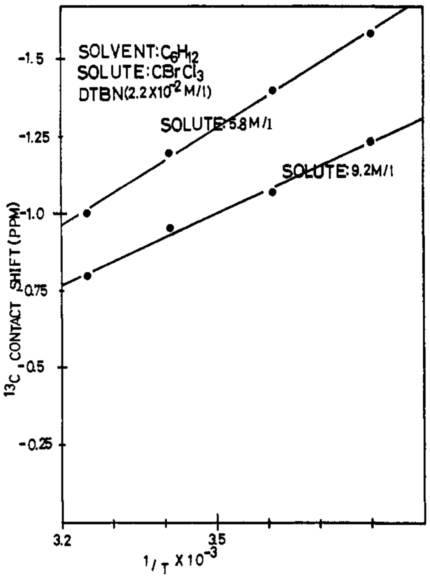

Figure 1. Curie law test of the ^{13}C contact shift for $CBrCl_3$.

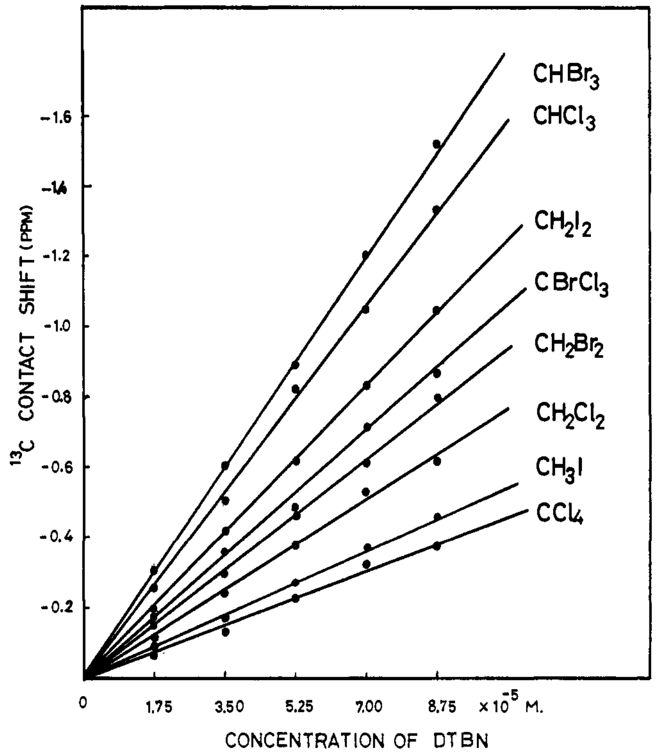

Figure 2. Observed ^{13}C contact shifts plotted against the concentration of DTBN.

eter equipped with the SD-HC heterospin decoupler and IS-60 field-frequency synchronous sweep system of the proton irradiating frequency. Spectra were measured with the external locking mode at various temperatures. ^{13}C chemical shifts were determined on an expanded scale (18 ppm per full scale) with the precision of ±0.10 ppm. Samples were made in the neat liquid or cyclohexane solution in the absence or presence of the given amount of DTBN in the 8-mm sample tube. The ^{13}C chemical shift of cyclohexane was hardly affected by the addition of DTBN within an experimental error and was used as an internal reference for ^{13}C chemical shift measurements of halogenated molecules in the presence of DTBN radical. The susceptibility shift was also too small to be measured. Samples used for the determination of the equilibrium constant were made in the cyclohexane solution with various concentrations. The concentration of added DTBN radical was varied from 0 to 2×10^{-4} *M*. The DTBN-induced ^{13}C contact shift is the shift change from the diamagnetic solution to the paramagnetic one in the presence of a given amount of DTBN.

Results and Discussion

Halomethanes. The addition of DTBN radical to neat CCl_4 and $CBrCl_3$ caused substantial downfield shift of the ^{13}C chemical shifts of these molecules. However, they were hardly affected by the addition of diamagnetic donor molecules such as pyridine and triethylamine. The temperature dependence of DTBN-induced ^{13}C shifts followed the Curie law behavior, characteristic of the Fermi contact shift (Figure 1). Therefore, the downfield ^{13}C shift induced addition of DTBN is most probably attributable to the Fermi contact shift, indicating positive spin density on the carbon s atomic orbital. We have also observed downfield ^{13}C shifts induced by the addition of DTBN for CHX_3 and CH_2X_2 molecules where X = Cl, Br, and I. The shifts were proportional to the concentration of added DTBN. Figure 2 shows the linear plots of the observed ^{13}C shifts of various halomethanes *vs.* the concentration of DTBN at room temperature. It is generally seen that the ^{13}C contact shifts for halomethanes are in the order of $X = I > Br > Cl$. However, slightly upfield proton contact shifts for CH_2X_2 and CHX_3 molecules were almost the same or in the opposite trend, $X = Cl > Br > I$. Previously we have reported[3,12] DTBN-induced ^1H and ^{13}C contact shifts for $CHCl_3$ and CH_2Cl_2 together with other proton donor molecules which were interpreted by the hydrogen bond between the C–H proton and the nitroxide oxygen or nitrogen.[12] Negative and positive spin densities on the proton and carbon, respectively, are induced by the spin polarization mechanism.[3,12] However, the above trend of the ^{13}C contact shifts for CHX_3 and CH_2X_2 ($X = I > Br > Cl$) is opposite to the hydrogen donor ability of these halomethanes. This suggests that C–X···DTBN interaction is important in these systems. As may be seen in Figure 2, $CBrCl_3$ shows even larger downfield ^{13}C contact shifts than CH_2X_2 (X = Cl and Br) molecules. Interaction here cannot involve the hydrogen bonding with DTBN. Therefore, the above observations immediately suggest the existence of an interaction between DTBN and halomethanes that is quite independent of any hydrogen bond. The ^{13}C contact shift behavior of solutions of halomethanes containing DTBN is that which would be expected if halomethanes form a CT complex with DTBN of the type C–X···DTBN. The CT character of halomethane–DTBN interaction can also be recognized experimentally (Figure 2) from the fact that the ^{13}C contact shift increases in the order $CBrCl_3 > CCl_4$ as might be expected. However, when we compare the results of CCl_4 and $CHCl_3$, the hydrogen bond with DTBN appears to be still important in the $CHCl_3$–DTBN system. For CHX_3 and CH_2X_2, both of the C–H···DTBN hydrogen bond and C–X···DTBN CT interactions could concurrently occur. The CT interaction could induce positive spin density by the spin delocalization mechanism[9] which permits electron spin transfer from DTBN directly to the antibonding orbital of the C–X bond. The C–H···DTBN hydrogen bond also induces positive spin density on the carbon by the spin polarization mechanism as has been

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(12) Paper VI: I. Morishima, K. Endo, and T. Yonezawa, *J. Chem. Phys.*, in press.

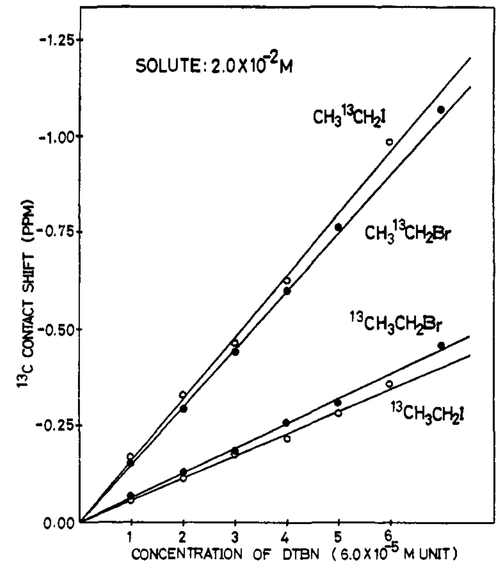

Figure 3. Observed ^{13}C contact shifts plotted against the concentration of DTBN for bromo- and iodoethanes.

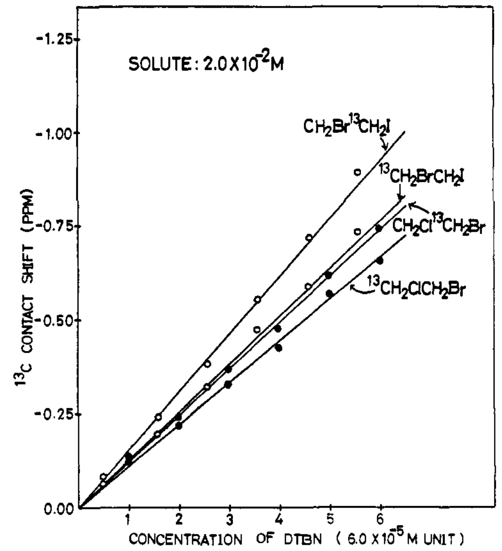

Figure 4. Observed ^{13}C contact shift plotted against the concentration of DTBN for 1,2-dihaloethanes.

revealed previously.[3,12] Therefore, the carbon of halomethanes senses positive spin density induced by the hydrogen bond and the CT interactions as in the following way.

$$\underset{\downarrow\ \uparrow}{\mathrm{DTBN\cdots H{-}C{-}X}} \quad \text{hydrogen bond (spin polarization)}$$

$$\underset{\uparrow\ \uparrow}{\mathrm{H{-}C{-}X\cdots DTBN}} \quad \text{charge-transfer interaction (spin delocalization)}$$

In order to substantiate further the CT nature of DTBN···halomethane interaction, we have measured the ^{19}F and ^{13}C contact shifts of CFCl$_3$ induced by the presence of DTBN. The downfield shifts of both nuclei may support the CT interaction stated above.[13]

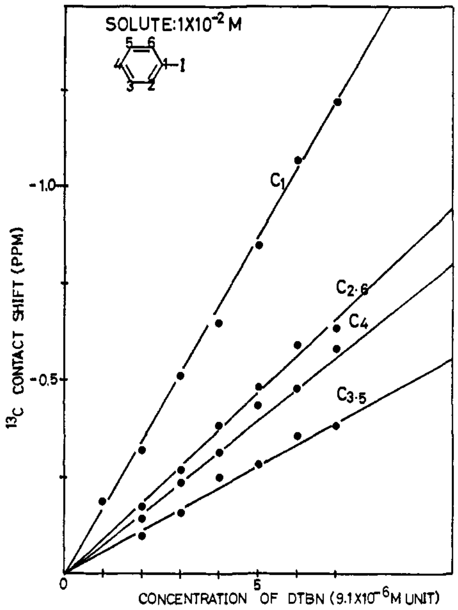

Figure 5. Observed ^{13}C contact shifts plotted against the concentration of DTBN for iodobenzene.

Haloethanes. Figures 3 and 4 show the plots of DTBN-induced ^{13}C contact shifts *vs.* the concentration of DTBN for several haloethane molecules. The downfield ^{13}C contact shifts for the methylene carbon in ethyl halides are more pronounced for iodide than for bromide, while that for the methyl carbon is greater for bromide than for iodide. This trend of the ^{13}C contact shifts in the methyl group is easily expected if the methyl C–H proton interacts with DTBN as a proton donor in the C–H···DTBN hydrogen bond; the C–H proton of the methyl group in ethyl bromide is more acidic and therefore more susceptible to the hydrogen bond with DTBN than ethyl iodide. On the other hand, the ^{13}C contact shifts in the methylene carbon bonded directly to the halogen atom follow the trend encountered for halomethanes in the order of ethyl iodide > ethyl bromide. The preferential interaction of the C–I group with DTBN was also recognized from the greater downfield contact shift of C$_2$ than C$_1$ in 1-bromo-2-iodoethane (see Figure 4). For 1-chloro-2-bromoethane, preferential downfield shift of C$_2$ was observed, as expected. In addition to this C–X···DTBN interaction, the C–H···DTBN hydrogen bond interaction could occur concurrently for 1,2-dihaloethanes. However, the results of the ^{13}C contact shifts for these haloethanes strongly suggest relative importance of the C–X···DTBN CT interaction.

Halobenzenes. We have also studied the ^{13}C contact shift for the halobenzene–DTBN system. Figures 5 and 6 show the DTBN-induced ^{13}C contact shifts for bromo- and iodobenzenes. The substituted carbon (C$_1$) of iodobenzene exhibits quite sensitively greater downfield contact shift than other ring carbons. On the other hand, the C$_1$ resonance of bromobenzene is quite insensitive to DTBN, compared with other ring carbons. This was also confirmed from the facts that in chlorobenzene the substituted C showed a slightly upfield DTBN-induced shift while the other C's exhibited substantial downfield shifts comparable with those in iodo- and bromobenzenes. These results show that the C–I···DTBN interaction in iodobenzene is important while in bromo- and chlorobenzenes the

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(13) We have observed the DTBN-induced ^{19}F nmr contact shift of CFCl$_3$ in 50 mol % CCl$_4$ solution using a Jeolco PS-100 spectrometer at 94.1 MHz. The addition of 1.5 × 10^{-5} *M* DTBN caused 0.15 ± 0.05 ppm downfield shift of the ^{19}F resonance for CFCl$_3$. The ^{13}C contact shift for the corresponding paramagnetic solution was 0.60 ± 0.10 ppm downfield shift.

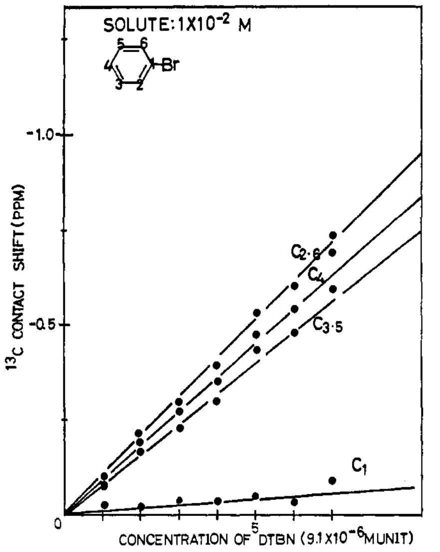
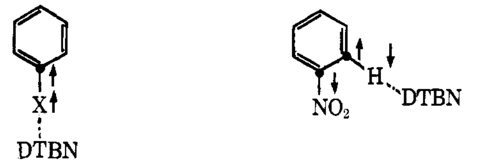


Figure 6. Observed ^{13}C contact shift plotted against the concentration of DTBN for bromobenzene.

C–H···DTBN hydrogen bond interaction is predominant. The fact that the aromatic C–H group can act as a proton donor to DTBN has previously been shown for various aromatic hydrocarbons.[14] The carbon of benzene exhibited substantial downfield ^{13}C contact shift by the addition of DTBN.[14] The aromatic carbon senses positive spin density induced by the C–H···DTBN hydrogen bond through the spin polarization mechanism.[14] The substituted carbon of nitrobenzene in which the nitro group is inert to DTBN showed *upfield* contact shift while other ring carbons exhibited usual downfield contact shifts (Figure 7). This upfield ^{13}C contact shift for C_1 in nitrobenzene is possibly due to the negative spin density induced by the C_1–C_2–H···DTBN interaction through the spin polarization mechanism (see below). Of course, in halobenzenes the C_2–H···DTBN hydrogen bond induces negative spin density on the substituted carbon and reduces positive spin density induced by the C_1–X···DTBN CT interaction. This is probably responsible for quite a small magnitude of downfield contact shift for C_1 of bromobenzene.



charge transfer interaction (spin delocalization) hydrogen bond interaction (spin polarization)

In chlorobenzene, positive and negative spin densities on C_1 induced by both interactions cancel; this appears to be responsible for the observation of a slightly upfield ^{13}C contact shift of the substituted C. In fluorobenzene, DTBN-induced ^{13}C shifts were quite similar to those in nitrobenzene; the substituted C was shifted upfield and other carbons were moved downfield. This finding implies the relative importance of the C_2–H···DTBN hydrogen bond compared with the C_1–F···DTBN interaction. In nitro- and fluorobenzenes with the electronegative substituent, the C_2–H bond is more acidic and susceptible to the hydrogen bond with DTBN, which induces negative spin density on the C_1. We have also measured the ^{19}F contact shift for fluorobenzene. The observed downfield ^{19}F contact shift may suggest that there is still weak CT interaction between the C–F bond and DTBN. These findings for halobenzenes correspond reasonably to the preferential donor–acceptor interaction between C–X bond and DTBN radical.

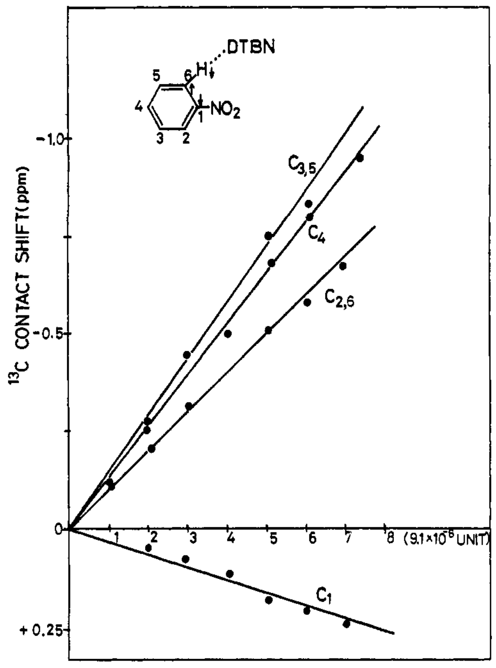


Figure 7. Observed ^{13}C contact shift plotted against the concentration of DTBN for nitrobenzene.

Equilibrium Constants and Limiting Contact Shifts. To facilitate a quantitative analysis of the interaction between DTBN radical and halogenated molecules, the formation constant, limiting contact shift, and spin density on the carbon are needed. There is a vast literature on the spectrophotometric study of weak CT complexes. For the 1:1 donor–acceptor complex formation between halomethane and DTBN with the condition of $[A]_0 \gg [D]_0$, the following linear equation is obtained[15]

$$1/\Delta = 1/K[D]_0\Delta_0 + [A]_0/[D]_0\Delta_0$$

where K is the formation constant, $[A]_0$ and $[D]_0$ are the initial concentration of electron acceptor (halomethane) and electron donor (DTBN), respectively, Δ_0 the limiting ^{13}C contact shift for the pure complex relative to the ^{13}C shift for the free halomethane, and Δ is the observed ^{13}C shift of halomethane in the presence of DTBN relative to the free halomethane. However, as shown by Person[16] and Deranleau,[17] simultaneous evaluation of K and Δ_0 values for weak complex formation is difficult and these values obtained from the above straight-line fitting procedure should contain substantial uncertainty. The separation of

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(14) Paper IV: I. Morishima, T. Matsui, T. Yonezawa, and K. Goto, *J. Chem. Soc., Perkin Trans. 2*, 633 (1972).

(15) R. Foster and C. A. Fyfe, "Progress in Nmr Spectroscopy," Vol. 4, Pergamon Press, Oxford, 1969.

(16) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

(17) D. A. Deranleau, *ibid.*, **91**, 4044 (1969).

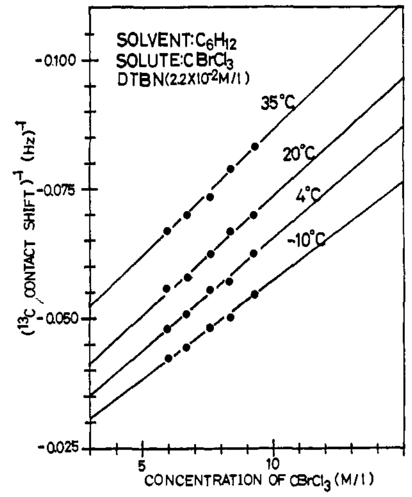

Figure 8. Plots of the inverse of the observed ^{13}C contact shifts against the initial concentration of $CBrCl_3$ at various temperatures.

K and Δ_0 requires special conditions that *K* is large and DTBN is completely complexed.[16,17] However, this is rarely possible. In this respect, we carried out only order estimation of *K* and Δ_0 values by the above standard procedure. Therefore, the results of *K* and the limiting ^{13}C contact shifts are not realistic when we use these values for a quantitative discussion.

Figure 8 shows the linear plots of $1/\Delta$ *vs.* the initial concentration of $CBrCl_3$, as an example, at various temperatures. The *K* values at various temperatures obtained from these linear plots lead to the heat of complex formation. The results are summarized in Table I. According to the critical works of Person and Deranleau, it is generally possible to make an error analysis of *K* and Δ_0. However, in our case where $[A]_0 \gg [D]_0$ and the signal of A is observed, the equations of Deranleau are not applicable. Therefore, the results in Table I may have serious uncertainty.[18] Only order of magnitude is important. It is likely that the observed trend of ^{13}C contact shifts for halomethanes results partly from the difference in *K* values and partly from the large difference in the limiting ^{13}C contact shifts. It is also probable that the ΔH values for adducts of the nitroxide radical with halomethanes appear to be not so different from those for the diamagnetic donor–acceptor interactions.[4–7]

Table I. Approximate Values of Formation Constant, Limiting ^{13}C Contact Shift, Heat of Complex Formation, and Spin Densities on the Carbon for CH_2Br_2 and $CBrCl_3$–DTBN Interactions

T, °K	*K*, l./mol[a]	ΔH, kcal/mol[b]	Limiting ^{13}C shift,[c] ppm	Spin density,[d] ρ_C
		CH_2Br_2		
306	0.28		−250	0.00102
293	0.38	−3.8	−280	0.00102
279	0.50		−300	0.00113
268	0.63		−310	0.00113
				Av 0.00108
		$CBrCl_3$		
308	0.12		−650	0.00270
293	0.14	−1.7	−710	0.00280
277	0.17		−740	0.00280
263	0.20		−810	0.00290
				Av 0.00280

[a] Uncertainty of the *K* value is ±0.20 l./mol at least. [b] Uncertainty of the ΔH value is at least ±2.5 kcal/mol. [c] Uncertainty of the limiting shift is at least 150 ppm. [d] Spin density on the carbon was obtained from the limiting ^{13}C contact shifts by using the equation, ($\Delta H/H = -a_C(\gamma_e g\beta S(S+1)/\gamma_c 3kT)$ where $a_C = 820.10\text{-}\rho_C$ (see ref 12 and 19).

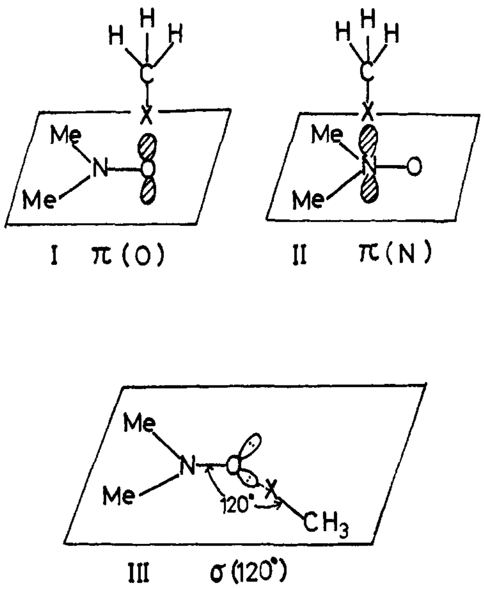

Figure 9. Models of the $CH_3X\cdots$DMNO bimolecular system with various configurations.

A Theoretical Study on the Halomethane–Dimethyl Nitroxide Bimolecular System by Molecular Orbital Calculations. In order to substantiate theoretically the DTBN-induced ^{13}C contact shift for halogenated molecules and to elucidate the nature of DTBN–halomethane interaction, we have performed unrestricted Hartree–Fock MO calculations (INDO-SCF method)[19] on the DMNO (dimethyl nitroxide)–halomethane bimolecular system. This type of MO calculation has been proved to be successful in reproducing spin densities and interaction energies for the proton donor–DMNO hydrogen bonding system. INDO-MO calculations were carried out here for the $H_3C\text{–}X\cdots$DMNO bimolecular system arranged in the three geometries (Figure 9).[20] In models I (π(O)) and II (π(N)), the C–X bond is placed perpendicularly over the $p\pi$ orbital of the oxygen and nitrogen atoms of DMNO, respectively, while in model III (σ(120°)) the C–X bond is placed on the σ plane and directed toward an oxygen lone-pair orbital (the N–O–X angle = 120°). We have examined fluoride and chloride for CH_3X in INDO calculations.

The results are summarized in Table II. Figures 10 and 11 show the stabilization energies varying with

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(18) According to Deranleau,[17] the limit for accurate simultaneous determination of *K* and Δ_0 constants is approximately $0.2 \leq s \leq 0.8$ where *s* is the saturation fraction and equivalent to $[AD]/[D]_0$ in the present case. However, in the present study we cannot estimate the *s* value.

(19) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

(20) The d orbitals are not considered in the INDO method even though these undoubtedly play a significant role in reality.

Table II. INDO–MO Calculations for the $CH_3X\cdots$Dimethyl Nitroxide Bimolecular System

Complex model	X	R, Å	ΔE,[a] kcal/mol	Calculated spin density on CH_3X $\rho_{C(2s)}$	$\rho_{X(2s)}$	$\rho_{H(1s)}$	a_N,[b] Gauss	Δq_C[c]	Δq_X[c]	$\Delta p_{CX(p-\sigma)}$[d]	$\Delta p_{CX(s-s)}$[d]
I π(O)	F	1.5	20.3	0.0369	0.0177	−0.0022	−3.15	+0.132	−0.291	−0.013	−0.026
	Cl	1.5	4.8	0.0249	0.0407	−0.0023	−2.50	+0.005	−0.007	−0.059	+0.027
II π(N)	F	1.5	6.0	0.0298	0.0169	−0.0007	+4.21	+0.187	−0.267	−0.004	−0.047
III σ(120°)	F	1.5	4.3	−0.0026	−0.0031	0.0004	+0.58	+0.152	+0.142	+0.217	−0.046

[a] $\Delta E = E - E_\infty$, the energy of stabilization. The R values are at the energy minimum. [b] The change of the a_N value for DMNO caused by $CH_3X\cdots$DMNO interaction. The plus and minus signs mean the increase and decrease in the a_N value, respectively. a_N was obtained by $a_N = 379.34\rho_{N(2s)}$ (ref 12). [c] Δq_C and Δq_X denote the change in the total charge densities on the carbon and halogen atoms in CH_3X. The plus and minus signs mean the increase and decrease in electron densities. [d] $\Delta p_{CX(p-\sigma)}$ and $\Delta p_{CX(s-s)}$ mean the change in the total p–σ and s–s bond orders for the C–X bond in CH_3X. The plus and minus signs mean the increase and decrease in the bond order.

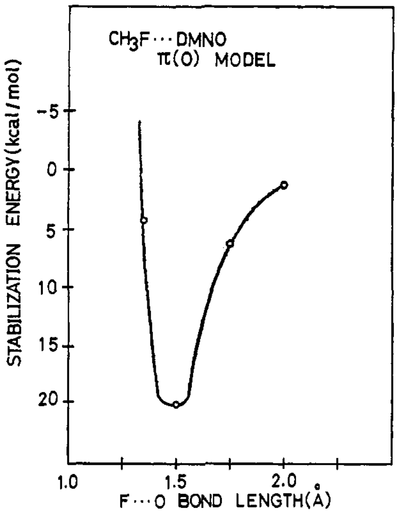

Figure 10. INDO stabilization energy curve plotted against the F···O distance for CH_3F–DMNO bimolecular system (the π(O) model).

X···O (or N) distance for methyl fluoride. The energy of stabilization, ΔE, was obtained at R (X···O (or N) distance) = 1.5 Å for most of the bimolecular systems. The results of calculated spin densities allow us to conclude that the π model is responsible for the downfield ^{13}C contact shift of halomethane interacting with DTBN. This is also the case for the hydrogen bond with DTBN.[3,12] Positive spin density is induced both on the X and C 2s atomic orbitals, which is possibly due to the electron spin transfer directly to the C–X antibonding orbital by the spin delocalization mechanism. This should be compared with the results for the case of the C–H···DMNO hydrogen bond in which negative and positive spin densities are induced on the proton and carbon s atomic orbitals by the spin polarization mechanisms.[3,12]

Quite a large value of the stabilization energy is obtained for the π(O) model of fluoromethane, compared with the other two models. However, when we use tentatively the input parameters (I_p, E_A, and β)[21] of chlorine in place of fluorine atom and other variables, such as various types of integrals in INDO method, are not varied, we obtain quite a reasonable value of the stabilization energy (4.8 kcal/mol), comparative with the experimental value. Spin density, on the other hand, appears to be rather insensitive to the above parametrization (Table II). Therefore, comparison between calculated stabilization energy and observed interaction energy is not realistic in the present case, but it seems worthwhile to compare the theoretical and experimental values of spin density on the carbon of CH_3X. Quite a small value of observed spin density on the carbon (Table I), compared with the theoretical value for the π(O) or the π(N) model, may allow us to expect the contribution of the σ(120°) model in addition to the π model; the σ model yields negative spin density on the carbon and diminishes the absolute value of the positive spin density. The importance of the σ model has also been encountered for the hydrogen bond between proton donor and nitroxide radical.[3,12] However, it should be noted that the π model is responsible for the observed value of the positive spin density on the carbon.

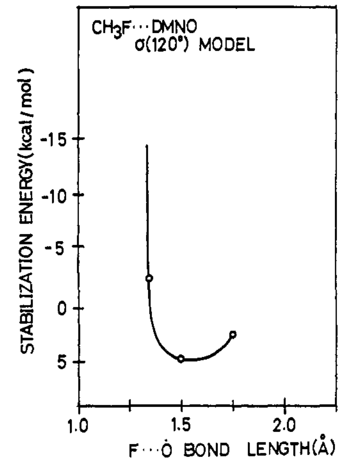

Figure 11. INDO stabilization energy curve plotted against the F···O distance for CH_3F bimolecular system (σ(120°) model).

Another feature of the results of INDO calculations (Table II) is that the hyperfine coupling constant of nitrogen, a_N, in DMNO is substantially affected by halide-DMNO interaction. The experimental study on the solvent effect of a_N showed that the a_N value is slightly increased on going from cyclohexane to CCl_4 or to $CBrCl_3$.[22] This trend is reproduced by the calculation for models II and III. Also in this sense, the contribution of the σ model should not be ignored.

Table II also contains the changes of charge density and bond order due to the C–X···DMNO complex

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[21] The UHF–INDO calculations including chlorine atom are not available in the original method.[19]

[22] We have studied the solvent effect of a_N of DTBN in the various halomethane solvents using Jeolco 3BX esr spectrometer with a 100-Kc modulation. The value of a_N increased slightly on going from CCl_4 (15.30 G) to $CBrCl_3$ (15.40 G). In both solvents a_N is larger than in cyclohexane (15.20 G). This trend of experimental results is in agreement with the Drago's recent work (ref 8).

formation. The results for the σ model show that total charge densities on the F and C atoms increase and s–s and p–σ bond order between C add F atoms decreases. This indicates that in the above complex formation halomethane accepts the electron into the antibonding orbital of the C–X bond, causing the weakening of the C–X bond. In fact, when DTBN was added to the solution of CHI_3, they reacted immediately and no esr signal was observed. For CH_2I_2 solution, this reaction was slow and the esr signal gradually disappeared. These results appear to correspond with the above interpretation of the charge-transfer interaction.

Finally we briefly comment on the charge-transfer interaction between free radical and halomethane in light of the mechanism of the halogen abstraction reaction. Recently it has been suggested[23] that the transition state of the halogen abstraction reaction process produces anionic character on the carbon from which the iodine is being removed.

$$\text{R–I} + \cdot\text{Rad} \longrightarrow [\overset{\delta-}{\text{R}}\cdots\text{I}\cdots\overset{\delta+}{\text{Rad}}] \longrightarrow \cdot\text{R} + \text{I–Rad}$$

The above scheme corresponds to the abovementioned charge-transfer model of the transition state in which an odd electron transfers to the antibonding orbital of the R–X bond, causing the release of the C–X bond.[24] The anionic character and release of the C–X bond was well reproduced by INDO–MO calculations for the model molecule, CH_3F. The failure to observe the esr spectrum and the ^{13}C contact shift of the CHI_3 + DTBN system may result from the strong CT interaction, leading to the iodine abstraction reaction. It has been shown by Fukui, *et al.*,[25] that the polarographic reduction potential of haloalkanes is connected with the energy of their lowest unoccupied σ level. The parallel relation between the DTBN-induced ^{13}C contact shift and reduction potential $(E_{1/2})$ $[CHBr_3\ (E_{1/2} = -0.64) > CHCl_3\ (-1.67),\ CH_2I_2\ (-1.12) > CH_2Br_2\ (-1.48) > CH_2Cl_2\ (-2.33)]$[25] also shows that the lowest unoccupied orbital is important in the DTBN–halomethane interaction.

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(23) W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969); W. C. Danen and R. L. Winter, *ibid.*, **93**, 716 (1971).

(24) A similar discussion along with the CT interaction has been made on the photochemical halogen abstraction reaction of halomethanes in the presence of amines using as the electron donor (see ref 4).

(25) K. Fukui, K. Morokuma, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **36**, 217 (1963).

Localized Charge Distributions. II. An Interpretation of the Barriers to Internal Rotation in H_2O_2[1]

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Abstract: The INDO geometry optimized H_2O_2 barriers are analyzed with localized molecular orbitals and findings from an earlier study of C_2H_6. Emphasis is placed on the slight delocalization of an orbital onto bonds coplanar with its largest amplitude and accompanying nodal properties. The cis barrier is found to arise from HH interferences in the OH orbitals. The trans barrier is found to arise from OO interferences in lone pairs roughly trans to OH bonds in the equilibrium molecule. An explanation for the incorrect INDO H_2O_2 frozen frame barrier is also offered.

Many theoretical studies[2–8] have been stimulated by the barriers to internal rotation in H_2O_2. The *ab initio* calculations[3–8] have undoubtedly been motivated by the fact that barriers and geometries were usually obtained that agreed poorly with experiment.[9,10] In fact, until the recent work of Veillard,[8] it was not clear that the barriers and conformation could be understood in the molecular orbital (MO) theory.[3–7] This, as pointed out by Veillard,[8] is surprising in the sense that H_2O_2 is the simplest molecule to exhibit an internal rotation barrier. However, Lowe[11] has shown that the high symmetry of a methyl rotor may force a great deal of error cancellation, and this would not occur in H_2O_2.

It is known[12,13] that both CNDO/2[14] and INDO[15]-SCF theory predict barriers and *optimized* geometries in

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(1) Work performed in the Ames Laboratory of the Atomic Energy Commission, Contribution No. 3001.

(2) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

(3) U. Kaldor and I. Shavitt, *ibid.*, **44**, 1823 (1966).

(4) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261, 2276 (1967).

(5) L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967).

(6) W. Palke and R. M. Pitzer, *ibid.*, **46**, 3948 (1967).

(7) R. M. Stevens, *ibid.*, **52**, 1397 (1970).

(8) A. Veillard, *Chem. Phys. Lett.*, **4**, 51 (1969); *Theor. Chim. Acta*, **18**, 21 (1970).

(9) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962).

(10) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, **42**, 1931 (1965).

(11) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 23 (1968).

(12) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).

(13) M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

(14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).