April, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 1267—1272 (1985)*

Environment Effects on the ESR Spectrum of the Cation Radical of Dimethylketene in Low Temperature Matrices

Jun Fujisawa, Shin Sato,* Kazuo Shimokoshi,† and Tadamasa Shida††
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
†*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*
††*Department of Chemistry, Kyoto University, Sakyo-ku, Kyoto 606*
(Received December 4, 1984)

The cation radical of dimethylketene produced in γ-irradiated solid solutions of various halocarbons has been investigated by ESR over a temperature range from 77 K to the melting point of each matrix. The cation radical in CCl_4 was stable up to about 180 K and the spectrum was well resolved to allow the determination of the anisotropic ESR parameters. In CCl_2FCClF_2 and CCl_2FCCl_2F, a series of irreversible spectral changes was observed with an increase in temperature. This process was interpreted in terms of the formation of the dimer cation. In the matrix of CCl_3F, the ESR spectrum exhibited extra structure, which varied reversibly with temperature. The analyses of the spectra suggested that the cation radical in CCl_3F weakly interacts with surrounding matrix molecules to form adducts.

The employment of a CCl_3F matrix for the radiolytic generation and stabilization of molecular cation radicals has been established and proved to yield ESR spectra with no serious interference by the matrix radicals.[1] Since a theoretical analysis of the spectrum without any consideration of the matrix usually gives satisfactory results, little attention has been paid to the matrix effect.

Other media such as SF_6,[2] CCl_2FCClF_2,[3] and CCl_3CF_3[4] have subsequently been found to also be useful. Use of these compounds along with CCl_3F revealed that the behavior of some cation radicals depends upon the matrix employed. For example, two types of thermal reactions of alkane cations occur depending upon the matrix.[5—7] It seems that in general, unimolecular reactions occur preferentially in CCl_3F and CCl_3CF_3, while bimolecular reactions through molecular diffusion are easy in SF_6 and CCl_2FCClF_2.[5—10]

Recently, we have examined the ESR spectra of dimethylketene cation radicals in several matrices over a wide range of temperatures, and found a drastic dependence of the spectrum upon the matrices. In the present contribution, we describe the results of detailed analyses of these ESR spectra and discuss the reactions occurring in the matrices to gain an insight into the matrix effect at low temperatures.

Experimental

Dimethylketene was kindly supplied by Dr. N. Washida of National Institute of Environmental Studies. After the purity was checked by gas chromatography, the compound was kept in liquid nitrogen to avoid polymerization. Other reagents including halocarbons (CCl_4, CCl_3F, CCl_2FCClF_2, and CCl_2FCCl_2F) from Tokyo Kasei Co. were used without further purification.

For the ESR measurement, dimethylketene was dissolved in each halocarbon to a concentration of 10^{-1}—10^{-3} in mole ratio, then degassed and sealed off in a Suprasil quartz tube. The samples, thus prepared, were γ-irradiated at 77 K to a dose of about 0.8 Mrad (1 Mrad=10^4 J kg^{-1}) to generate the cation radicals. The ESR spectra were recorded on a JES FE-2XG spectrometer at 77 K and higher temperatures. The ESR parameters of cation radicals were determined using a proton magnetic-resonance probe and a digital frequency counter (Takeda Riken Co. TR 5211C).

Results and Discussion

Determination of Anisotropic ESR Parameters. As was briefly described in a previous paper,[11] singly occupied molecular orbitals of cation radicals of ketenes are characterized mainly by $\pi_{C=C}$ (π orbital on C=C bond), similar to olefin cation,[8] rather than by $n_{C=O}$ (lone pair orbital on C=O bond) as in the case of aldehyde and ketone cations.[12—14] The dimethylketene cation showed a nearly isotropic septet spectrum by the hyperfine interactions of six equivalent methyl protons (23.0 G (1 G=1×10^{-4} T)). In this section, the results of our further investigations with the use of CCl_4 as matrix are presented.

Though the CCl_4 matrix has been employed for the optical absorption study of various radical cations,[15] it is not generally used for ESR studies because the concomitantly produced radicals such as CCl_3 and CCl_4^+ are bothersome.[16] However, the spectrum of dimethylketene cation obtained for the solution in CCl_4 at 153 K (Fig. 1a) is not interfered with by the by-products and is highly resolved. This indicates that the local magnetic environment of the cation radical in CCl_4 varies little from site to site and that the line width of the underlying absorption of the by-products is much broader than that of the septet lines.

The spectral pattern of the septet is essentially the same as that found in our previous results,[11] but it may be noticed that there are slight splittings due to an anisotropy in the outermost component at low field. Thus, we performed a simulation of the ESR line shape for powder samples.[17] Figure 1b represents the best fit spectrum calculated by the use of the parameters listed in Table 1. From the excellent agreement between Figs. 1a and 1b, it is concluded that the hyperfine interaction of methyl protons in dimethylketene cation is slightly anisotropic. The parameters determined in this way are also applicable to the cation radicals in other matrices, which will be discussed later.

Dimerization Reaction. The ESR spectra of a

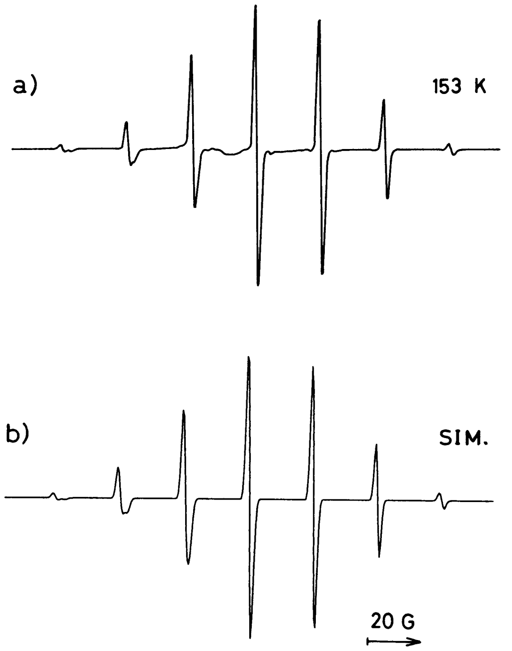


Fig. 1. (a) ESR spectrum of dimethylketene cation in CCl_4 at 153 K; (b) Simulation for (a) using the parameters given in Table 1 and a line width, $\Delta H_{msl}=1.6$ G, of Gaussian line.

TABLE 1. ESR PARAMETERS FOR THE DIMETHYLKETENE RADICAL CATION IN CCl_4 AT 153 K

components of g tensor and g_{iso}	^{1}H hyperfine couplings, G
$g_{\parallel}=2.0028$	$A_{\parallel}=22.75$
$g_{\perp}=2.0037$	$A_{\perp}=23.62$
$g_{iso}=2.0034$	$A_{iso}(6H)=23.33$

dimethylketene cation in CCl_2FCClF_2 or CCl_2FCCl_2F exhibited additional small subpeaks even at 77 K.[11] The intensities were dependent upon the concentration. Figures 2a and 2b demonstrate the spectra observed for CCl_2FCClF_2 solutions with $10^{-3}$and 10^{-2} mole ratio of dimethylketene, respectively. These figures show that at lower concentrations the subpeaks are suppressed. Even in this case, however, strong subpeaks appeared by keeping the sample at 77 K overnight after γ-irradiation. These results suggest that subpeaks are due to the species formed by a reaction of dimethylketene cation with a neutral molecule of dimethylketene. Figure 2c represents the simulated spectrum for Fig. 2b. The simulation was obtained by assuming a composite of a septet (I) of dimethylketene cation and a nonet (II) as indicated by the stick diagram. The good agreement indicates the coexistence of the nonet (II) whose g factor and sum of the coupling constants are identical to those of septet (I) (17.3 GX8= 23.1 GX6).

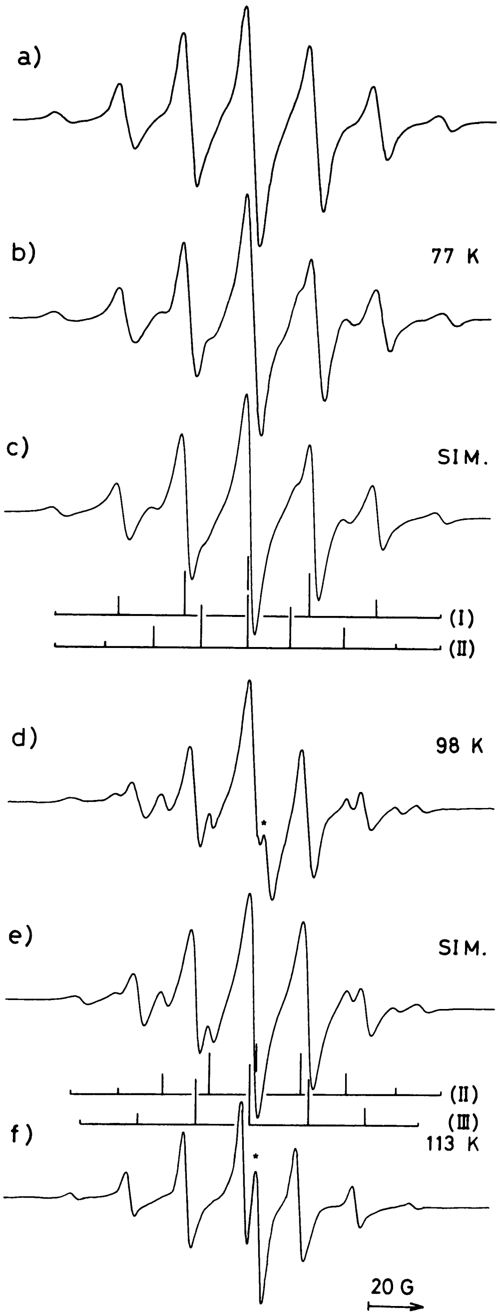


Fig. 2. ESR spectra of (a) 0.1 mol%; (b), (d), (f) 1.0 mol% solutions of dimethylketene in CCl_2FCClF_2 at (a), (b) 77 K; (d) 98K; (f) 133K after γ-irradiation at 77 K; (c) Simulation for (b) assuming the abundance ratio of 1.00 to 0.15 for $(CH_3)_2CCO^+$ (I) and $((CH_3)_2CCO)_2^+$ (II) respectively; (e) Simulation for (d) assuming the abundance ratio of 0.20 to 1.00 for $((CH_3)_2CCO)_2^+$ (II) and $(CH_3)_4C_4O_2^+$ (III) respectively. The ESR parameters of (I)—(III) are listed in Table 2. The asterisk indicates the transition due to the matrix radicals.

Upon warming, the spectral feature of this system changed completely; *i.e.*, a series of irreversible change was observed. Figure 2d shows the observed spectrum at 98 K, which again can be decomposed into two components demonstrated by the stick diagrams under Fig. 2e. One is the nonet (II) mentioned above and the other is a new septet (III) with a splitting of 20.5 G which is slightly smaller than that of (I). It is noteworthy that this septet shows a considerably large positive shift of g factor. Further elevation of temperature results in the disappearence of the nonet

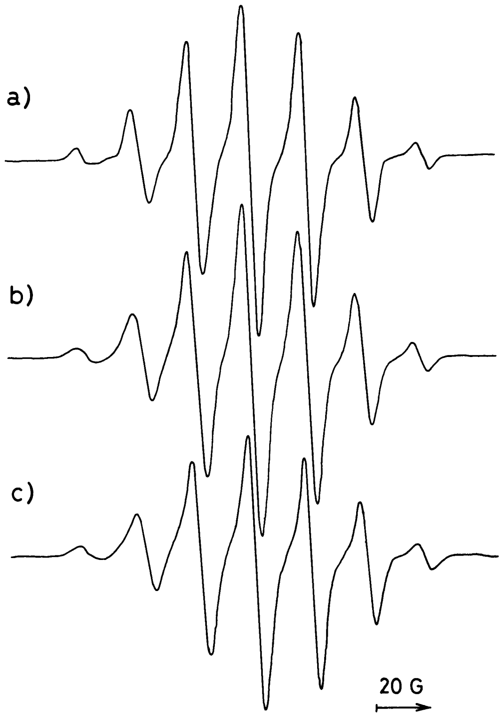


Fig. 3. ESR spectra of (a) CCl_3F; (b) CCl_2FCClF_2; (c) CCl_2FCCl_2F solutions of dimethylketene dimer measured at 77 K after γ-irradiation at 77 K, showing features assigned to $(CH_3)_4C_4O_2^+$.

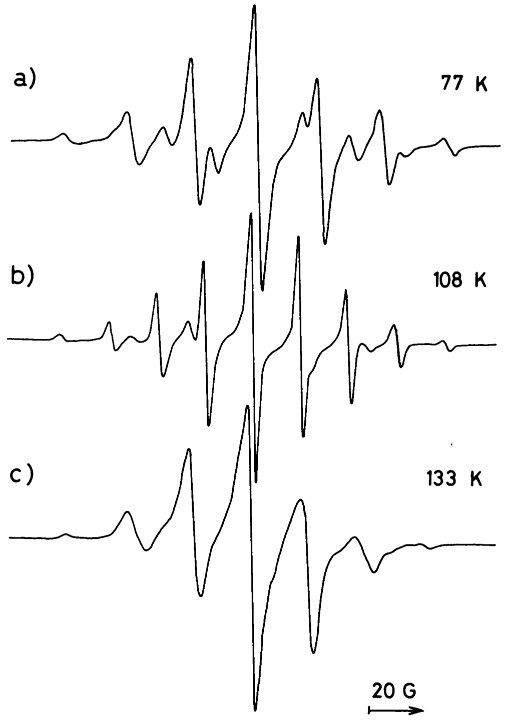


Fig. 4. ESR spectra of CCl_2FCCl_2F solution of dimethylketene measured at (a) 77 K; (b) 108 K; (c) 133 K after γ-irradiation at 77 K. Main features of these spectra are assigned to $(CH_3)_2CCO^+$ (I) ($((CH_3)_2CCO)_2^+$) (II), and $(CH_3)_4C_4O_2^+$ (III), respectively.

Table 2. ESR parameters for the observed spectra in CCl_2FCClF_2 and CCl_2FCCl_2F

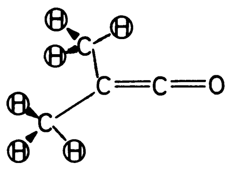
Spectrum	Species	Matrix	g_{iso}	A_{iso}(G)
(I)	$(CH_3)_2CCO^+$	CCl_2FCClF_2	2.0034	23.1 (6H)
		CCl_2FCCl_2F	2.0034	23.0 (6H)
(II)		CCl_2FCClF_2	2.0034	17.3 (8H)
		CCl_2FCCl_2F	2.0034	17.3 (8H)
(III)		CCl_2FCClF_2	2.0043	20.5 (6H)
		CCl_2FCCl_2F	2.0044	20.4 (6H)
	[a] $(CH_3)_4C_4O_2^+$	CCl_2FCClF_2	2.0041	20.4 (6H)
		CCl_2FCCl_2F	2.0041	20.4 (6H)

a) Formed from dimethylketene dimer by positive charge transfer.

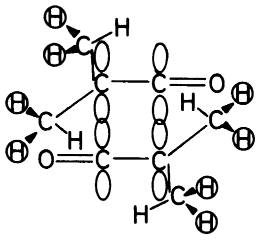
(II) to give exclusively the septet spectrum (III) (Fig. 2f). In order to elucidate the mechanism for the sequence of spectral changes, it is necessary to identify (II) and (III). We carefully examined a variety of candidates for the septet (III) in Fig. 2f in literatures, but no one agreed with the observed spectrum. On the other hand, we found (experimentally) a system which gives a very similar spectrum to (III). The system is the γ-irradiated Freon solution of dimethylketene dimer (2,2,4,4-tetramethyl-1,3-cyclobutanedione), $(CH_3)_4C_4O_2$. The spectra observed for the three Freon solutions are shown in Fig. 3 (see also, Fig. 4c). The ESR parameters of this spectrum are comparable with those obtained from the spectrum (III) (Table 2), although the line width of the septet in Fig. 2f is slightly smaller than those in Figs. 3 and 4c.

On the basis of above assignment, the spectral change observed in Fig. 2 may be explained in the following manner. Septet (I) is associated with the isolated dimethylketene cation, which is presumed to have a C_{2v} symmetry with six magnetically equivalent rapidly rotating methyl protons (Structure I). Upon the elevation of temperature from 77 to 98 K, molecular diffu-

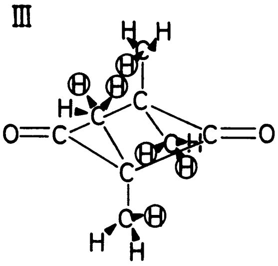
I



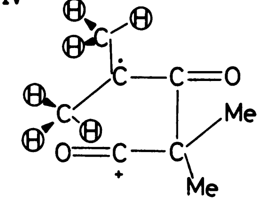
II



III



IV



sion and/or reorientation may take place to produce a dimer cation, a possible conformation being shown in Structure II. If the rotation of the methyl groups is hindered to make the eight encircled protons in Structure II magnetically equivalent, we may associate the nonet (II) underlying in Figs. 2b and 2d with this dimer cation of dimethylketene. Such a dimer cation has been observed for tetramethylethylene;[18] the spectrum is characterized by a 25-line pattern, the splitting constant of which is one half that of the 13-line pattern of the monomer cation. Since the spectrum changed from a septet to a nonet in the present case, it is provisionally assumed that the methyl groups in the dimer cation are fixed in a restricted conformation and only eight protons participate in the revelation of the 9-line hyperfine structure. The fact that the g factor and the sum of coupling constants are common to both spectra (I) and (II) indicates the similarity of electronic structure between the two species and suggests that the spectral change from (I) to (II) corresponds only to the change in the number of the protons giving rise to the observed hyperfine splitting.

Further elevation of temperature yields another septet (III) in Fig. 2f which is attributed to a cation radical of dimethylketene dimer. As for the structure of the cation radical, there are two possibilities; one is the symmetric structure III in which six encircled protons are assumed to be magnetically equivalent. The other is the ring opened structure IV.[19]

Essentially the same spectral change as in Figs. 2a—f was observed for the matrix of CCl_2FCCl_2F as shown in Fig. 4. In this case, the nonet associated with the dimer cation was observed unambiguously at 108 K. The observed ESR parameters in CCl_2FCCl_2F are summarized in Table 2 along with those obtained in CCl_2-$FCClF_2$.

Cation-matrix Interaction. Different behavior of dimethylketene cation was found in the case of CCl_3F matrix. Figure 5a shows the observed spectrum of the cation in CCl_3F at 77 K. The overall features of the septet due to the monomer cation of dimethylketene are similar to those observed in other matrices, except for the small peaks flanking each component of the septet.

The extra structure might be considered as due to the anisotropy of the proton hyperfine splitting. However, any reasonable set of parameters of anisotropy for the protons could not yield comparable simulation spectra. On the other hand, we found that, if the extra structure in Fig. 5a is ignored, the rest of the spectrum can be reproduced by using the anisotropic parameters determined in the previous section. Figure 5b shows the spectrum thus calculated. The variation of line widths for individual components is well reproduced. The substructure, therefore, cannot be attributed to the anisotropy of the spectrum. Moreover, the warming of the system caused a drastic and reversible change of the substructure as shown in Fig. 6. Such a change cannot be associated with a simple motional averaging of anisotropy. Examination of Fig. 6 reveals that the substructure which is barely seen at 77 K is emphasized on warming, and the triplet feature of each component of the septet changes to a doublet (see also, Fig. 7).

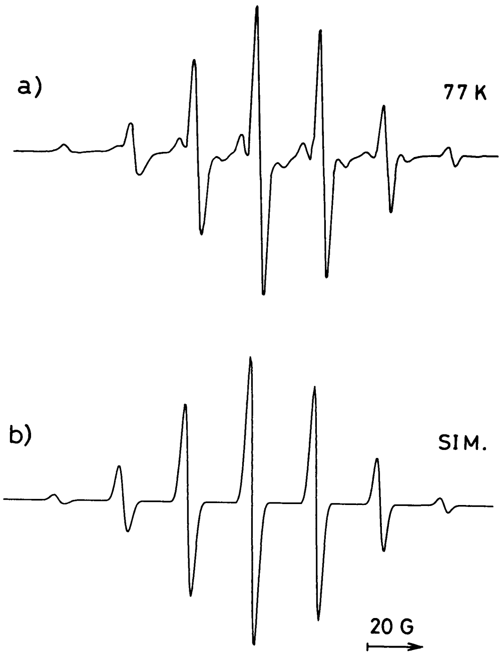


Fig. 5. (a) ESR spectrum of dimethylketene cation in CCl_3F at 77 K; (b) Simulation for (a) using the parameters given in Table 1 and a line width, $\Delta H_{msl}=3.0$ G.

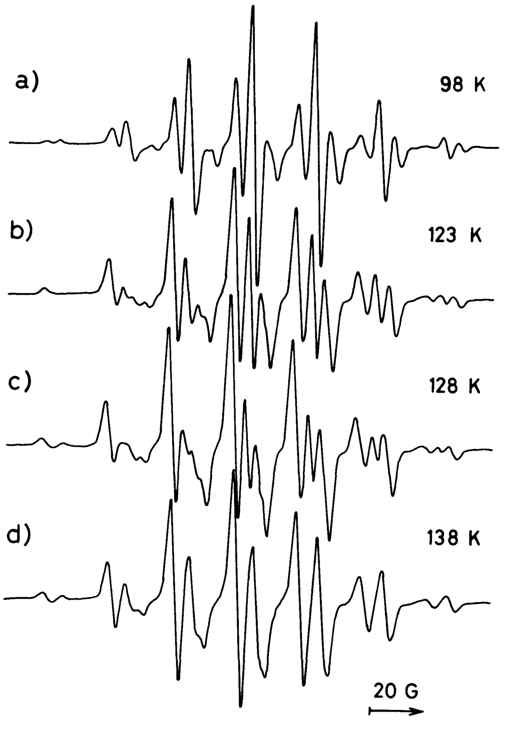


Fig. 6. ESR spectra of dimethylketene cation in CCl_3F at (a) 98 K; (b) 123 K; (c) 128 K; (d) 138 K after γ-irradiation at 77 K, showing the reversible change of substructures with temperature.

Thus, the temperature dependence of the spectra observed in CCl_3F is quite different from that observed

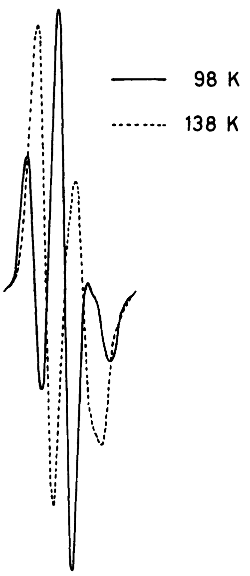


Fig. 7. The central part of the spectra of dimethylketene cation in CCl_3F recorded at 98 K (solid line) and 138 K (dotted line).

in CCl_2FCClF_2 or CCl_2FCCl_2F and evidently cannot be explained in terms of the bimolecular reaction. In addition, the perturbation causing the extra structure should not be strong, because the proton ESR parameters previously determined in the CCl_4 matrix are applicable to the present system with a good accuracy. A weak interaction between the cation and surrounding matrix molecules is conceivable. In the case of CCl_3F, the chlorine ($I=3/2$) or the fluorine ($I=1/2$) atom can cause a superhyperfine interaction. The latter seems to be more probable from the spectral features and the fact that no substructure was observed with CCl_4. Since the fluorine nucleus has a large hyperfine coupling ($A_{iso}=17160$ G for $\rho_{2s}=1$),[20] a very small spin density is enough to give the observed extra structure.

From this point of view, we attempted to simulate the observed spectra using ESR parameters in Table 1 plus the assumption that there are additional nuclei with $I=1/2$ in the system. In Figs. 8 and 9, we show the spectra obtained after repeated curve fittings to those observed at 98 and 138 K, respectively. The existence of two equivalent nuclei with splitting constants of $A_{\parallel}=8.0$ G and $A_{\perp}=4.2$ G for Fig. 8b and one nucleus with $A_{\parallel}=12.0$ G and $A_{\perp}=3.5$ G for Fig. 9b was assumed. The agreement between each pair of spectrum is satisfactory. Such a large anisotropy of the extra interaction is compatible with the involvement of the fluorine atom.

We tested various values of the g factor and the proton anisotropic hyperfine coupling constant. However, a slight change in the parameters (from those listed in Table 1) caused a remarkable deviation from the observed spectra and no improved spectra could be obtained. This indicates that the proton ESR parameters in Table 1 are valid whether there is a superhyperfine interaction or not, which, in turn, allows us to estimate the superhyperfine coupling constants. The fact that we needed two sets of the superhyperfine parameters for the different temperatures may indicate that either the intermolecular complex or the mechanism of the interaction is different between the two temperatures. However, the attempt to reproduce the spectra observed in the intermediate range of the temperature by a simple superposition of the three spectra (Figs. 5b, 8b, and 9b), was not successful. Some dynamic process such as

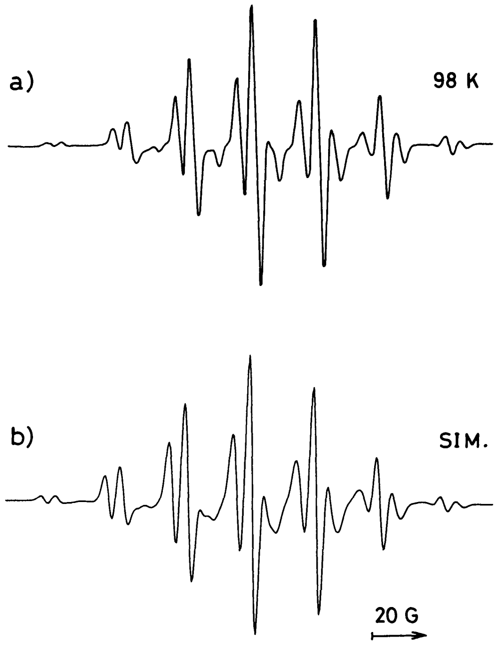


Fig. 8. (a) ESR spectrum of dimethylketene cation in CCl_3F at 98 K; (b) Simulation for (a) using the parameters given in Table 1 for protons in the cation and $A_{\parallel}=8.0$ G, $A_{\perp}=4.2$ G for two fluorine nuclei in the matrix molecules interacting with the cation.

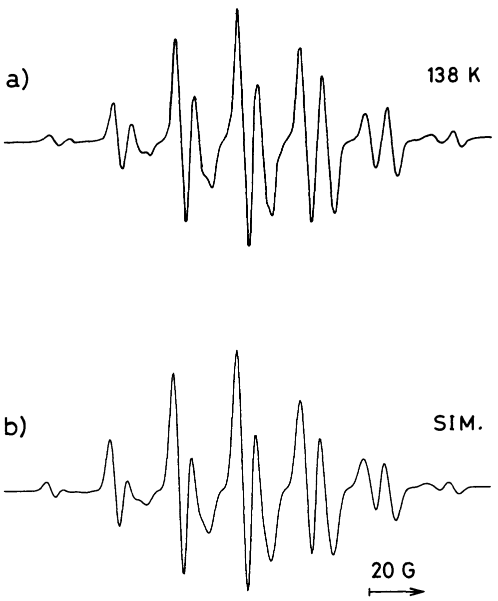


Fig. 9. (a) ESR spectrum of dimethylketene cation in CCl_3F at 138 K; (b) Simulation for (a) using the parameters given in Table 1 for protons and $A_{\parallel}=12.0$ G, $A_{\perp}=3.5$ G for one fluorine nucleus.

the line alternation effect resulting from the spin exchange[21] might be related to the observed spectral change.

The superhyperfine interaction has been discussed for several cations in the matrix, in particular, in CCl_3F.[22–29] In most cases, the cations exhibit superhyperfine structures which change reversibly with the temperature. For example, the cation radical of acetaldehyde shows such behavior. Two different interpretations have been proposed for this reversibility. One is the motional averaging of the anisotropy[25] and the other is a reversible thermal dissociation.[14,26] The complete analysis of the spectral change with temperature in relation to the dynamical process is subject to further study.

References

1) T. Shida, H. Kubodera, and Y. Egawa, *Chem. Phys. Lett.*, **79**, 179 (1981).

2) M. Iwasaki, K. Toriyama, and K. Nunome, *J. Am. Chem. Soc.*, **103**, 3591 (1981).

3) K. Toriyama, K. Nunome, and M. Iwasaki, *J. Phys. Chem.*, **85**, 2149 (1981).

4) M. Tabata and A. Lund, *Z. Naturforsch.*, **38a**, 428 (1983).

5) K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, **77**, 5891 (1982).

6) M. Iwasaki, K. Toriyama, and K. Nunome, *Rad. Phys. Chem.*, **21**, 147 (1983).

7) K. Nunome, K. Toriyama, and M. Iwasaki, *Chem. Phys. Lett.*, **105**, 414 (1984).

8) T. Shida, Y. Egawa, H. Kubodera, and T. Kato, *J. Chem. Phys.*, **73**, 5963 (1980).

9) K. Ushida and T. Shida, *J. Am. Chem. Soc.*, **104**, 7332 (1982).

10) M. Tabata and A. Lund, *Rad. Phys. Chem.*, **23**, 545 (1984).

11) K. Shimokoshi, J. Fujisawa, K. Nakamura, S. Sato, and T. Shida, *Chem. Phys. Lett.*, **99**, 483 (1983).

12) M. C. R. Symons and P. J. Boon, *Chem. Phys. Lett.*, **89**, 516 (1982).

13) L. D. Snow and F. Williams, *J. Chem. Soc., Chem. Commun.*, **1983**, 1090.

14) P. J. Boon, M. C. R. Symons, K. Ushida, and T. Shida, *J. Chem. Soc., Perkin Trans. 2*, 1213 (1984).

15) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

16) T. Shida and Y. Takemura, *Rad. Phys. Chem.*, **21**, 157 (1983).

17) K. Shimokoshi, *Bull. Chem. Soc. Jpn.*, **51**, 635 (1978).

18) T. Ichikawa and P. K. Ludwig, *J. Am. Chem. Soc.*, **91**, 1023 (1969).

19) Our preliminary experiment at 4 K seems to favor the second possibility.

20) J. R. Morton and K. F. Preston, *J. Magn. Res.*, **30**, 577 (1978).

21) C. A. McDowell and K. Shimokoshi, *J. Chem. Phys.*, **60**, 1619 (1974).

22) A. Hasegawa and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, **79**, 93 (1983).

23) D. Becker, K. Plante, and M. D. Sevilla, *J. Phys. Chem.*, **87**, 1648 (1983).

24) L. D. Snow and F. Williams, *Chem. Phys. Lett.*, **100**, 193 (1983).

25) L. D. Snow and F. Williams, *Chem. Phys. Lett.*, **100**, 198 (1983).

26) M. C. R. Symons and P. J. Boon, *Chem. Phys. Lett.*, **100**, 203 (1983).

27) G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons, and A. Hasegawa, *J. Chem. Res (S).*, 258 (1983).

28) M. Iwasaki, H. Muto, K. Toriyama, and K. Nunome, *Chem. Phys. Lett.*, **105**, 586 (1984).

29) J. Rideout and M. C. R. Symons, *J. Chem. Res(S).*, 268 (1984).