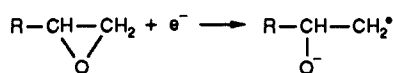


Na⁰(epoxy)₁₋₃ Complexes and Dissociative Electron Capture of the Epoxy System: Matrix Isolation ESR Study

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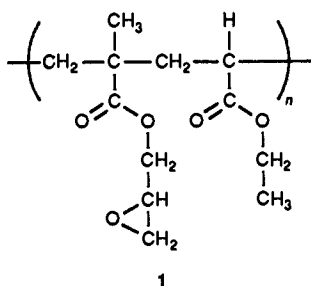
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Abstract: It is postulated that a high electron beam sensitivity of epoxyated poly(meth)acrylate results from the dissociative electron capture by the epoxy moiety.

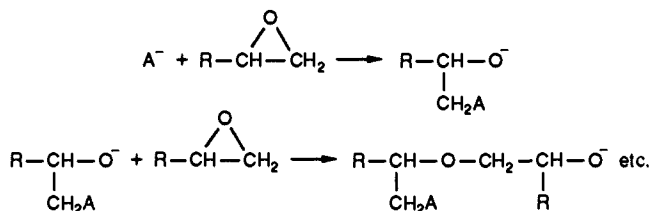


Na atoms and epoxy molecules (ethylene oxide, trimethylene oxide, and tetrahydrofuran) were cocondensed in argon matrices, and the Na-to-epoxy electron transfer was induced by mild radiation ($\lambda > 580$ nm). ESR examination of the matrices demonstrated that ethylene oxide and trimethylene oxide, but not tetrahydrofuran, readily captured low-energy electrons, and the resulting anions had the structure consistent with the postulated ring opening. The conformations of the radical anions were determined from the α and β proton hyperfine coupling tensors. The ESR study also revealed the formation of (epoxy)₁₋₃Na⁰ complexes upon cocondensation of Na atoms and the epoxy molecules examined in argon matrices. Spectral analyses revealed that these complexes were formed through dative interaction of the oxygen lone pair electrons with the vacant Na orbitals, and the unpaired electron was in an sp hybridized orbital of the Na atom pointing away from the ligand(s).

Epoxyated poly(meth)acrylate such as glycidyl methacrylate-ethyl acrylate copolymer **1** is exceptionally sensitive toward electron beam and is widely used as an electron beam negative resist in microlithography.^{1,2} The sensitivity of nominal

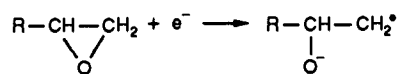


poly(meth)acrylate (as measured in terms of G value) is less than 1/10 of the copolymer **1**; the sensitivity of the latter is hence attributed to its epoxy moiety. A generally accepted mechanism is that an electron beam somehow generates a base, and it, in turn, initiates a well-known base-catalyzed polymerization process of ethylene oxide.³ Instability of small cyclic ether (ethylene oxide and trimethylene oxide) toward nucleophilic attack is well-known and is attributed to the ring strain.



When a beam of high-energy electrons passes through a medium, the most numerous event is ionization. It has been shown that when the energy of the primary beam is above ~ 10 KeV, the total number of free electrons generated in the medium through cascading ionization processes is $\sim 10^3$ times that of the primary

electrons.⁴ Most of them are in the thermal energy range. We postulated that the high sensitivity of the epoxy system toward an electron beam might be due to the direct reaction between the epoxy system and a low-energy electron as depicted below. The



resulting free-radical terminus can either initiate the chain reaction of the epoxy system or cross-link with another radical terminus. In order to substantiate the postulated mechanism we decided to examine which cyclic ethers, if any, would capture an electron in a neutral environment, and whether the anion, if formed, had the structure resulting from the ring-opening process.

The technique of cocondensing metal atoms of low ionization potential (e.g., Na atoms) and molecules with some electron affinity in an argon matrix and effecting electron transfer between them by mild radiation, thus generating *chemically isolated* metal cations and molecular anions in the matrix, had been demonstrated and described many years ago.⁵ The mild radiation required for the electron transfer ($\lambda > 580$ nm in the case of Na atoms) ensures that the electron being captured is indeed that of thermal energy, and neither the starting acceptors nor resulting anions are subjected to photoradiation of consequence. This report presents the result of such a matrix isolation, photoinduced electron-transfer study conducted to examine the electron affinity of epoxy system and to determine the structure of the anion, if formed, by using ESR spectroscopy. The Na atoms were chosen as electron donors.

Soon after we began the project, we learned that (epoxy)₁₋₃Na⁰ complexes were formed upon cocondensation of the Na atoms and epoxy molecules in argon matrices. The epoxy molecules examined were ethylene oxide, trimethylene oxide, and tetrahydrofuran. Di-*n*-propyl ether was also examined. All the epoxy molecules formed the Na⁰(epoxy)₁₋₃ complexes. Di-*n*-propyl ether formed only the mono and diligand complexes. The spectral analyses revealed that these complexes were formed through dative interaction of the oxygen lone pair electrons with the vacant Na orbitals, and the unpaired electron was in an sp hybridized orbital of Na pointing away from the ligand(s).

The envisaged Na-to-epoxy electron transfer with mild radiation ($\lambda = 600 \pm 50$ nm) was indeed observed in the cases of ethylene oxide and trimethylene oxide. The electron transfer occurred not

(1) Thompson, L. F.; Feit, E. D.; Heidenreich, R. D. *Polymer Eng. Sci.* **1974**, *14*, 529.

(2) Thompson, L. F.; Ballantyne, J. P.; Feit, E. D. *J. Vac. Sci. Technol.* **1975**, *12*, 1280.

(3) See, for example, a chapter by Wilson, C. G. in *Introduction to Microlithography*; Thompson, L. F.; Willson, C. G.; Bowden, M. Eds.; American Chemical Society: Washington, D.C., 1983; pp 128-130.

(4) Parikh, M. J. *Chem. Phys.* **1980**, *73*, 93.

(5) Kasai, P. H. *Acc. Chem. Res.* **1971**, *4*, 329.

only from the isolated metal atoms but also within the complexes, and the resulting anions had the ring-opened structures as postulated. The conformations of the anions were determined through careful simulation of the spectra based on the α and β proton hyperfine coupling tensors. The corresponding Na-to-ether electron transfer was not observed with tetrahydrofuran nor with di-*n*-propyl ether.

Experimental Section

An ESR spectrometer-cryostat assembly that would permit trapping of vaporized metal atoms in argon matrices at near liquid helium temperature and examination of the resulting matrices by ESR has been described earlier.⁵ In the present series of experiments Na atoms were vaporized from a resistively heated stainless steel tube ($\sim 250^\circ\text{C}$) and were trapped in argon matrices containing controlled amount (1–3 mol %) of epoxy molecules.

The ESR spectrometer used was an IBM instruments ER200D system. All the spectra reported here were observed, while the matrices were maintained at $\sim 4\text{ K}$. The spectrometer frequency was 9.415 GHz. For photoirradiation of the matrix a high-pressure xenon-Hg lamp (Oriel, 1 KW unit) was used. The light beam was passed through a water filter and a broad band ($\pm 50\text{ nm}$) interference filter of choice and was focussed on the cold-finger $\sim 40\text{ cm}$ away.

Trimethylene oxide, 3,3-dimethyloxetane, tetrahydrofuran, and di-*n*-propyl ether were obtained from Aldrich Chemical Company and were mixed with research grade argon from Matheson Gas Products. An ethylene oxide(1%)–argon mixture was obtained from Scott Specialty Gases.

Spectra and Assignments

Trimethylene Oxide. For the sake of clarity we shall first present the result obtained from trimethylene oxide. Figure 1 (parts a and b, respectively) shows the ESR spectrum observed from an argon matrix containing Na atoms only and that observed from an argon matrix in which the Na atoms and trimethylene oxide (2%) had been cocondensed. The ESR spectrum of Na atoms condensed in an argon matrix had been studied earlier by Jen et al.⁶ The spectrum seen in Figure 1a is due to isolated Na atoms ($3s^1$); the quartet pattern with the average spacing of 330 G is due to the hyperfine interaction with the ^{23}Na nucleus ($I = 3/2$, natural abundance = 100%, $\mu = 2.2174\beta_n$). Splittings within each hyperfine components are due to multiple trapping sites; two sites, one with the largest hyperfine coupling interaction (hence presumably with the least perturbation) and the other with the smallest hyperfine coupling interaction (hence with the largest perturbation), are most conspicuous.

In Figure 1b the letter A indicates the quartet due to isolated Na atoms. Other than several weak signals clustered about the position corresponding to $g = 2.00$, all the additional signals were recognized as those of three, overlapping quartets, B, C, and D as indicated. These quartet patterns must surely be due to hyperfine interactions with the ^{23}Na nucleus. The doublet-like splitting of the B signals is ascribed to the multiple site effect; the relative intensity of the two components varied from one matrix to another, and it appeared to parallel the relative intensity of the isolated Na atoms at the two major trapping sites. Though the line widths of individual components of the quartets B, C, and D are significantly broader than those of isolated Na atoms, all the resonance positions of these signals were given accurately (within $\pm 1\text{ G}$) by the isotropic spin Hamiltonian (eq 1). Though

$$\mathcal{H}_{\text{spin}} = g\beta H \cdot S + A I \cdot S \quad (1)$$

significantly smaller than the atomic value, the ^{23}Na coupling constants of these quartets indicate a substantial unpaired electron density in the Na 3s orbital in each case. No hyperfine structures due to protons were resolved in any of the signals. These quartets thus could not be attributed to ion-pair radicals of the form $\text{Na}^+(\text{epoxy})_n^-$ where the unpaired electron density would essentially be all in the epoxy moiety.

The quartets B, C, and D were hence assigned to Na atoms complexed with one, two, and three epoxy molecules, $\text{Na}^0(\text{epoxy})_{1-3}$, respectively.

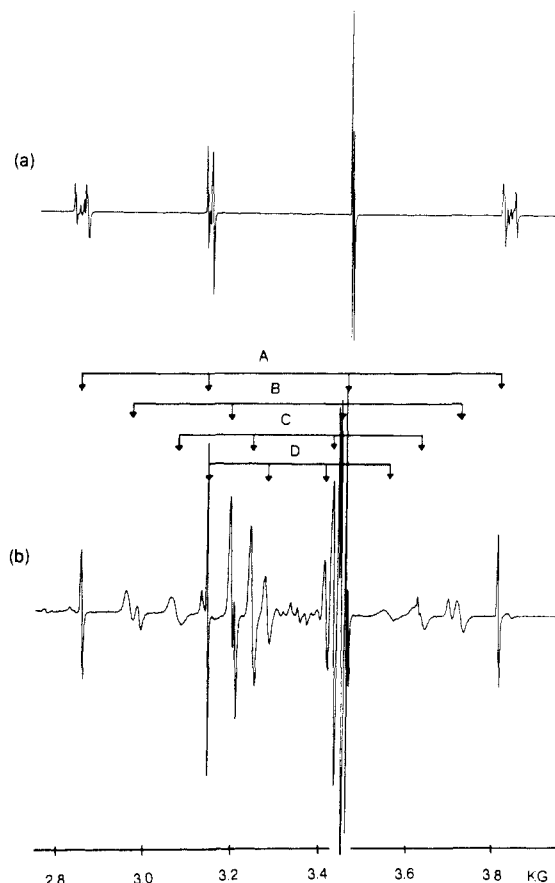


Figure 1. (a) ESR spectrum of the Na/Ar system. The signals due to isolated Na atoms ($I = 3/2$) at two major trapping sites are conspicuously seen. (b) ESR spectrum of the Na/trimethylene oxide(2%)/Ar system. The letter A indicates the quartet due to isolated Na atoms. The letters B, C, and D indicate the quartets assigned to (trimethylene oxide)₁₋₃Na⁰ complexes, respectively.

oxy)₁₋₃, respectively. The complexes are formed by the dative interaction of the oxygen lone pair electrons with the vacant valence orbitals of Na, and the unpaired electron is in an sp hybridized orbital of Na pointing away from the ligand(s).⁷ Decrease of the isotropic hyperfine interaction with the Na nucleus in the order of B, C, and D and increase in the line width of individual hyperfine components in the same order are thus attributed to the decrease of the 3s character and associated increase of the 3p character of the semifilled orbital with increasing number of epoxy molecules. The g values and the $A_{\text{iso}}(^{23}\text{Na})$ coupling constants of the $\text{Na}^0(\text{trimethylene oxide})_{1-3}$ complexes are listed in Table I.

Figure 2a shows, in an expanded scale, the central section of Figure 1b encompassing the inner two hyperfine components of the isolated Na atoms. The letters indicate to which quartets each individual signal belongs. In preparing the matrices of this type it is difficult to reproduce the Na concentration accurately. The concentration of epoxy molecules can be controlled and reproduced accurately. According to the proposed assignments of these quartets, the intensity ratios $[C]/[B]$ and $[D]/[B]$ should be independent of the Na concentration but are proportional to the first power and the second power of the epoxy concentration, respectively. The intensity ratios $[C]/[B]$ and $[D]/[B]$ given by the apparent heights of the second hyperfine components (those at left in Figure 2a) of the spectra of matrices containing 1, 2, and 3 mol % trimethylene oxide are shown in Table II. The observed ratios $[C]/[B]$ and $[D]/[B]$ indeed increased in proportion to the first power and the second power of the epoxy concentration in substantiation of the assignments.

Irradiation of the matrices showing the signals of isolated Na atoms and $\text{Na}^0(\text{trimethylene oxide})_{1-3}$ with yellow light ($\lambda = 600 \pm 50\text{ nm}$) for 4 min resulted in complete disappearance of these signals and appearance of a set of new, strong signals closely and

(6) Jen, C. K.; Bowers, E. L.; Cochran, E. L.; Foner, S. N. *Phys. Rev.* **1962**, *126*, 1749.

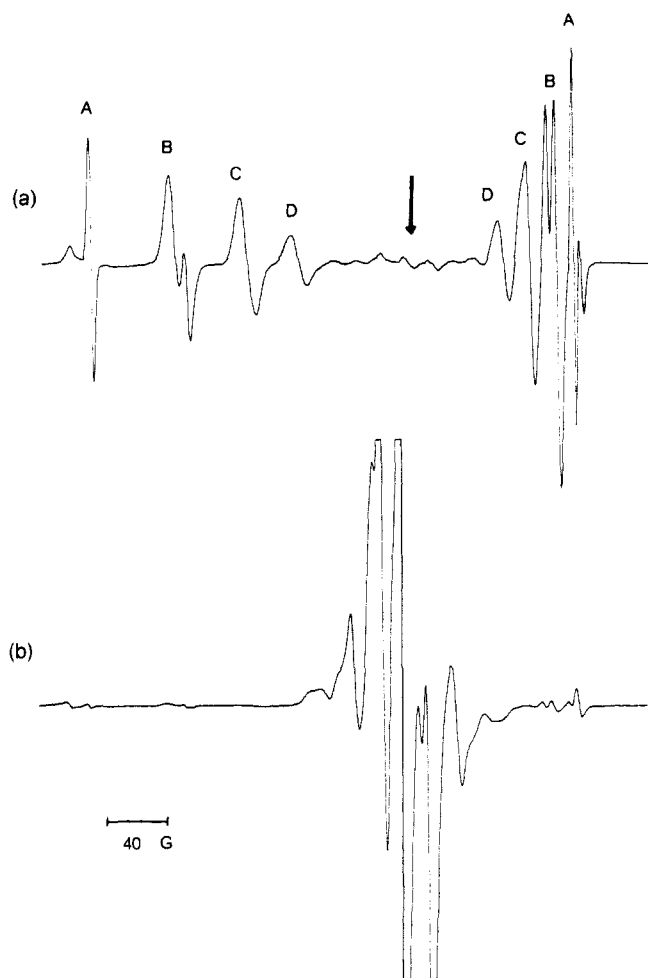
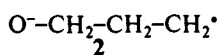


Figure 2. (a) The central section of Figure 1b shown in an expanded scale. The letters A, B, C, and D indicate the quartets each signals belong (see Figure 1b), and the arrow indicates the position corresponding to $g = 2.00$. (b) Same as (a) except observed after irradiation with yellow light ($\lambda = 600 \pm 50$ nm).

symmetrically placed about the position corresponding to $g = 2.00$. See Figure 2b. The new spectrum observed with a reduced gain in an expanded scale is shown in Figure 3a. Hyperfine structures attributable to the ²³Na nucleus is no longer present. The overall quintet pattern indicated in the figure was best accounted for by the hyperfine interactions of equal magnitude with four protons; the very weak signals seen outside the quintet pattern were believed to belong to the conformational isomer discussed later. The new spectrum was hence assigned to the trimethylene oxide anion of the ring-opened structure **2**. The α and β protons would be the



four protons responsible for the quintet pattern. That the two β protons have the equal hyperfine coupling constants close to those of the α protons intimates a certain conformation of the β methylene group relative to the α sector.

Most intriguingly when the matrix showing the spectrum Figure 3a was subsequently irradiated with blue light ($\lambda = 400 \pm 50$ nm) for 10 min, the spectrum changed to that shown in Figure 3b. The latter spectrum was recognized as a doublet-of-doublet-of-triplet as indicated. The observed change could be accounted for by a change in the conformation of the anion radical resulting in a large change of the β proton coupling constants. Detailed analyses of the conformation and spectral patterns of the anion radical **2** are presented in the Discussion section.

The envisaged Na-to-epoxy electron transfer thus appeared to occur not only from the isolated metal atoms but also within the complexes. For the usual photoinduced electron transfer between Na atoms and acceptor molecules isolated in argon matrices, the

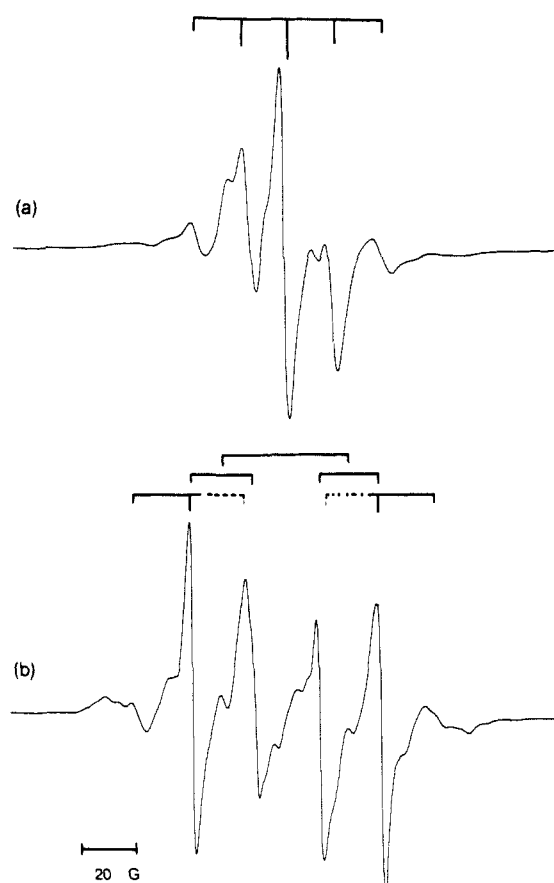
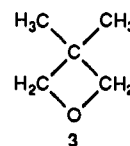


Figure 3. (a) ESR spectrum of trimethylene oxide anion. The indicated quintet pattern is attributed to the α and β protons of the ring-opened form. (b) ESR spectrum of the same matrix observed after subsequent irradiation with blue light ($\lambda = 400 \pm 50$ nm). The new spectrum (a doublet-of-doublet-of-triplet) is assigned to a conformational isomer of the same anion.

minimum photoenergy required is that corresponding to the Na D ($3s \rightarrow 3p$) transition at 589 nm. It follows that, for Na⁰(trimethylene oxide)₁₋₃ with its unpaired electron in an sp hybridized orbital of the Na atom, the required minimum photoenergy would be red-shifted. A systematic study indeed revealed that irradiation with red light (800 ± 50 nm) was sufficient to remove the signals due to Na⁰(trimethylene oxide)₃. Subsequent exposure of the matrix to 700 ± 50 nm light and to 650 ± 50 nm light removed the signals due to Na⁰(trimethylene oxide)₂ and Na⁰(trimethylene oxide)₁, respectively. Yellow light (600 ± 50 nm) was required to remove the remaining signals due to the isolated Na atoms. The signals due to anion radical **2** increased concurrently at each stage.

3,3-Dimethyloxetane. In order to obtain further substantiation of the spectral assignment of the trimethylene oxide anion, the experiment was repeated by using 3,3-dimethyloxetane, **3**. An



argon matrix in which Na atoms and 3,3-dimethyloxetane (2%) had been cocondensed showed an ESR spectrum which was essentially identical with that observed from the Na/trimethylene oxide/Ar system. The g values and the ²³Na hyperfine coupling constants of the Na⁰(3,3-dimethyloxetane)₁₋₃ complexes determined from the spectrum are included in Table I.

As expected, upon irradiation of the matrix with yellow light (600 ± 50 nm), all the signals due to isolated Na atoms and the complexes disappeared, and a new intense spectrum appeared symmetrically placed about the $g = 2.00$ position (Figure 4a).

Table I. *g* Values and ^{23}Na Nuclear Hyperfine Coupling Constants (in MHz) of $\text{Na}^{(0)}(\text{epoxy})_{1-3}$ Complexes^a

complex	$\text{Na}(\text{epoxy})_1^b$	$\text{Na}(\text{epoxy})_2$	$\text{Na}(\text{epoxy})_3$
ethylene oxide			
<i>g</i> =	1.9985		
<i>A</i> =	744		
trimethylene oxide			
<i>g</i> =	1.9986	1.9981	1.9979
<i>A</i> =	697	519	377
dimethyl oxetane			
<i>g</i> =	1.9996	2.0000	1.9991
<i>A</i> =	695	517	374
tetrahydrofuran			
<i>g</i> =	1.9991	1.9988	1.9979
<i>A</i> =	716	534	376
di- <i>n</i> -propyl ether			
<i>g</i> =	1.9997	1.9989	
<i>A</i> =	716	545	
isolated Na atoms at the least perturbed site			
<i>g</i> =	1.9991		
<i>A</i> =	928		

^aAccuracies are ± 0.0006 for *g* values and ± 3 MHz for *A*. ^bFor $\text{Na}(\text{epoxy})_1$ values reported are for those at the least perturbed site.

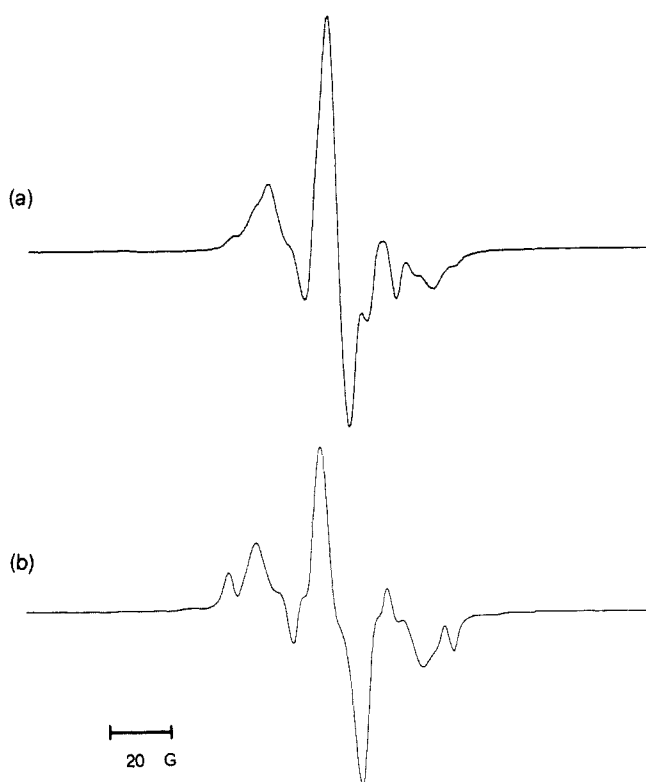
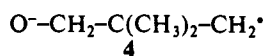


Figure 4. (a) ESR spectrum of 3,3-dimethyloxetane anion observed after photoirradiation of the Na/3,3-dimethyloxetane(2%)/Ar system with yellow light ($\lambda = 600 \pm 50$ nm). (b) ESR spectrum of same matrix observed after subsequent irradiation with blue light ($\lambda = 400 \pm 50$ nm).

The overall triplet pattern of the new spectrum could be readily accounted for by the anion radical of the ring-opened form 4.



Here only the α protons would have hyperfine coupling constants of consequence. Subsequent irradiation of the matrix with blue light (400 ± 50 nm) resulted in a small but distinct change of the spectrum (Figure 4b). It must signify a conformational change and some contribution of the methyl protons to the subtle features of the spectrum. The dominant triplet pattern due to the α protons remained unaltered.

Ethylene Oxide. The ESR spectrum observed from an argon matrix in which Na atoms and ethylene oxide (1%) had been

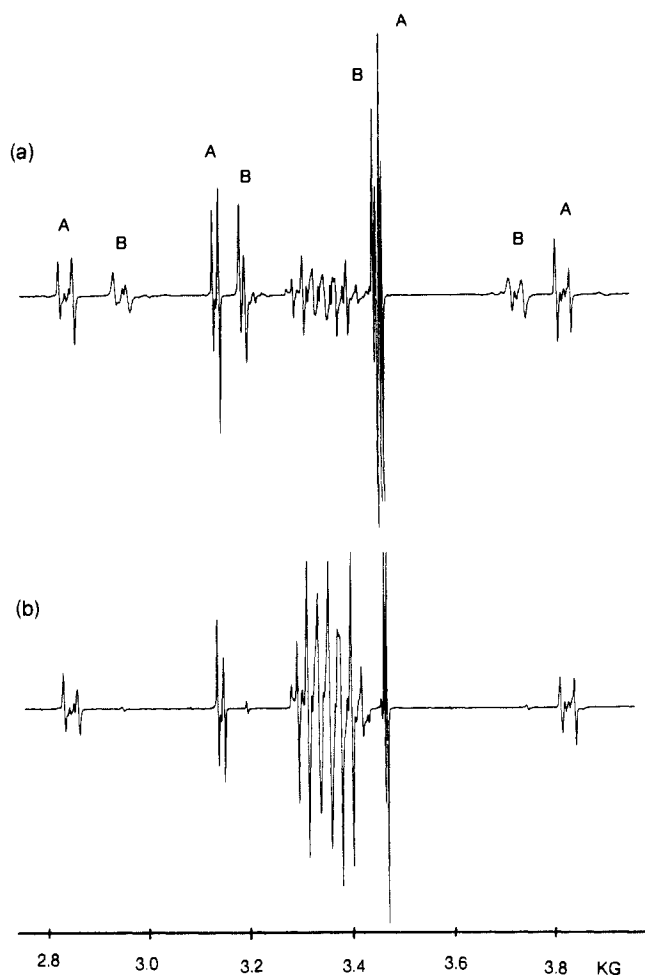


Figure 5. (a) ESR spectrum of the Na/ethylene oxide(1%)/Ar system prior to irradiation. The letters A and B indicate the quartets due to isolated Na atoms and (ethylene oxide)₁Na⁰ complexes, respectively. (b) ESR spectrum of same matrix observed after irradiation with $\lambda = 700 \pm 50$ nm light.

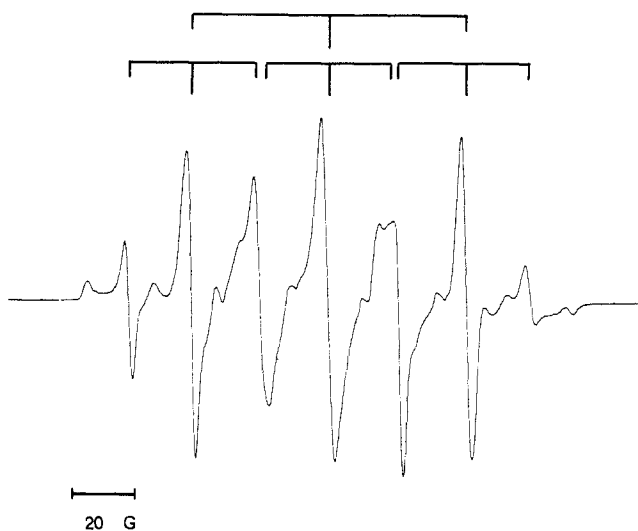


Figure 6. ESR spectrum of ethylene oxide anion of the ring-opened form. A triplet-of-triplet pattern is recognized as indicated.

cocondensed is shown in Figure 5a. The signals due to isolated Na atoms and mono(ethylene oxide) complexes (the B quartet) at two major trapping sites are readily recognized. Contrary to the results obtained with trimethylene oxide, no evidence is seen for the formation of the bis- and tris(ethylene oxide) complexes, and there is already a set of signals of significant intensity closely and symmetrically placed about the $g = 2.00$ position. Figure 5b shows the spectrum observed after the matrix above had been

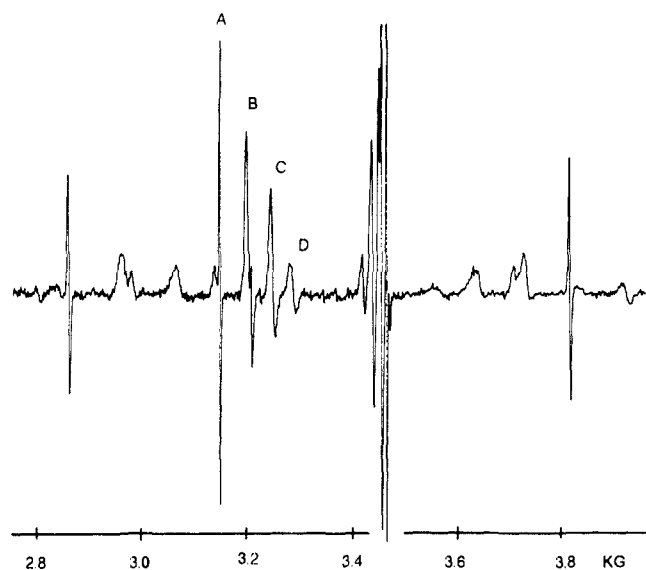


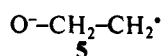
Figure 7. ESR spectrum of Na/tetrahydrofuran(2%)/Ar system. The isolated Na atoms and complexes formed are indicated in the second hyperfine group.

Table II. Relative Intensity Ratios [Na(epoxy)₂]/[Na(epoxy)₁] and [Na(epoxy)₃]/[Na(epoxy)₁] Observed with Trimethylene Oxide and Tetrahydrofuran^a

epoxy concentration	1%	2%	3%
[Na(TMO) ₂]/[Na(TMO) ₁]	0.29	0.71	0.92
[Na(TMO) ₃]/[Na(TMO) ₁]	0.07	0.31	0.59
[Na(THF) ₂]/[Na(THF) ₁]	0.33	0.65	
[Na(THF) ₃]/[Na(THF) ₁]	0.06	0.22	

^aThe peak-to-peak heights were used for the present purpose.

irradiated with 700 ± 50 nm light for 5 min. Disappearance of the signals due to Na⁰(ethylene oxide) and concurrent increase of the central signals are clearly demonstrated. Irradiation with 600 ± 50 nm light removed the remaining signals due to isolated Na atoms. The central spectrum is shown in Figure 6 in an expanded scale. The spectrum was recognized as a triplet-of-triplet as indicated and was assigned to the anion radical of the ring-opened form 5.



The electronic affinity of ethylene oxide must be such that, in the dispositions of the metal atom and the ligand molecules for the Na⁰(epoxy)_{2,3} complexes, the electron transfer occurs spontaneously from the Na atom to one of the ligand molecules. The *g* values and the *A*_{iso}(²³Na) value of the (ethylene oxide)₁Na⁰ complex are given in Table I. Detailed analyses of the spectrum and conformation of the anion radical 5 are given in the Discussion section.

Tetrahydrofuran. Figure 7 shows the ESR spectrum observed from the Na/tetrahydrofuran(2%)/Ar system. The formation of the (tetrahydrofuran)₁₋₃Na⁰ complexes in the matrix is evident. The *g* values and the *A*_{iso}(²³Na) values of these complexes are given in Table I. Since all three complexes were observed, the intensity ratios [C]/[B] and [D]/[B] were determined from the spectra observed from matrices containing 1 and 2 mol % tetrahydrofuran, respectively. The results are included in Table II.

In spite of the similarity of the spectrum in Figure 7 to that observed from the Na/trimethylene oxide(2%)/Ar system (Figure 1b), the only spectral change noted when the matrix was irradiated with yellow light ($\lambda = 600 \pm 50$ nm) was diminution of the signals of the Na atoms at the most perturbed sites and corresponding increase of the signals of the complexes. It is thus concluded that tetrahydrofuran does not undergo the dissociative electron capture process demonstrated by the smaller members of the cyclic ethers.

Di-*n*-propyl Ether. The ESR spectrum observed from the Na/di-*n*-propyl ether(2%)/Ar system is shown in Figure 8. The

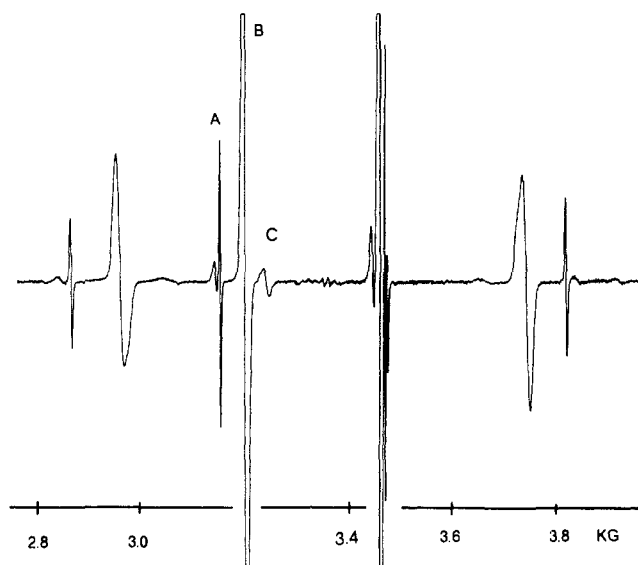


Figure 8. ESR spectrum of Na/di-*n*-propyl ether(2%)/Ar system. The isolated Na atoms and complexes formed are indicated in the second hyperfine group.

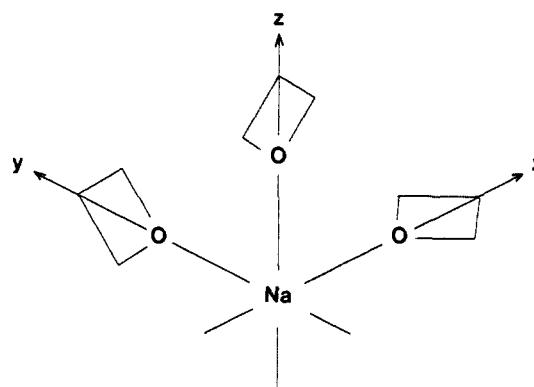


Figure 9. Structures of Na⁰(trimethylene oxide)₁₋₃ assumed for molecular orbital calculations. The Na-O distance of 2 Å and the known structure of trimethylene oxide were assumed.

spectrum shows the facility with which (di-*n*-propyl ether)₁Na⁰ is formed. The concentration of (di-*n*-propyl ether)₂Na⁰ is small, however, and (di-*n*-propyl ether)₃Na⁰ is totally absent. The spectrum remained unchanged when the matrix was irradiated with yellow light ($\lambda = 600 \pm 50$ nm). The *g* values and the *A*_{iso}(²³Na) values of Na⁰(di-*n*-propyl ether)_{1,2} are included in Table I.

Discussion

The ESR spectra of the Na⁰(epoxy)₁₋₃ complexes obtained above do not permit further elaboration of their structures. As stated earlier, the large unpaired electron density in the Na 3s orbital of these complexes indicates that the bonding scheme most likely responsible for their formation is the dative interaction of the oxygen lone pair electrons with the vacant Na 3p orbital(s). We hence performed EHT (extended Hückel theory) calculations⁸ of the (trimethylene oxide)₁₋₃Na⁰ complexes assuming (1) the known, essentially planar structure of trimethylene oxide,⁹ (2) the Na-O distance of 2 Å, and (3) the orientations of the necessary number of trimethylene oxide molecules along the *x*, *y*, and *z* axes as shown in Figure 9. In each case the calculation yielded the semifilled orbital of an *sp* hybridized orbital of the Na atom pointing away from the ligands. The unpaired electron distri-

(7) Similar interactions have been observed between Li atoms and water and ammonia molecules trapped in argon matrices. Meier, P. F.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* 1978, 100, 2108.

(8) Hoffmann, R. *J. Chem. Phys.* 1963, 39, 1397.

(9) Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* 1961, 34, 1319.

Table III. Unpaired Electron Distributions in Na(trimethylene oxide)₁₋₃ Given by EHT Calculations and $\rho(\text{Na}, 3s)$ Determined from Observed HF Coupling Constants

complex	$\rho(\text{Na}, 3s)$	$\rho(\text{Na}, 3p_x)$	$\rho(\text{Na}, 3p_y)$	$\rho(\text{Na}, 3p_z)$	$\rho(\text{Na}, 3s)_{\text{obsd}}$
Na(TMO) ₁	0.78	0.22			0.75
Na(TMO) ₂	0.60	0.18	0.18		0.56
Na(TMO) ₃	0.45	0.15	0.15	0.15	0.41

butions in the three complexes given by the EHT calculations are shown in Table III. The unpaired electron density in the Na 3s orbital determined from the observed $A_{\text{iso}}(^{23}\text{Na})$ values of the complexes and the isolated Na atoms are also shown in the table. The agreement between the observed and calculated unpaired electron densities in the Na 3s orbital is gratifying and renders further support to the spectral assignments and the postulated bonding scheme.

The ring-ruptured anions of trimethylene oxide and ethylene oxide, **2** and **5**, are both basically primary alkyl radicals. The unpaired electron is localized in the p_x orbital of the α carbon. The ESR spectra of these radicals are hence determined primarily by the hyperfine coupling tensors of the α and β protons.

The hyperfine coupling tensor of an α proton of an alkyl radical is well understood and typically assumes the following form.^{10,11}

$$A_{\parallel} = 12 \text{ G}, \quad A_{\perp, \parallel} = 22 \text{ G}, \quad A_{\perp, \perp} = 35 \text{ G} \quad (2)$$

Here, $A_{\perp, \parallel}$, for example, is the principal element of the coupling tensor measured perpendicular to the C-H bond but parallel to the p_x orbital of the α carbon. It is pertinent to note that, as the orientations of the coupling tensors of the two α protons differ by $\sim 120^\circ$ about the p_x orbital, the two protons would not always be equivalent in a given magnetic field. This inequivalency is manifested as an extra broadening of the central component of the triplet normally expected from the two protons with equal hyperfine coupling constants. The effect would diminish if the two protons interchange their positions either through rotation or by tunnelling.

A computer program that would simulate the ESR powder pattern of a radical having multiplet sets of hyperfine coupling tensors of differing orientations has been described earlier.¹¹ The effect of interchanging a particular pair of protons can be addressed by using the method of modified Bloch equation.^{12,13} Figure 10 shows the ESR powder patterns of an alkyl radical, RCH_2^\bullet , simulated based on an isotropic g tensor, the hyperfine interactions with two α protons with assumed $\text{H}_\alpha\text{-C}_\alpha\text{-H}_\alpha$ angle of 120° , and an interchange of the α protons at the rate of 0, 20, and 40 MHz. We may conclude that the central peak of the triplet due to the two α protons become prominent only when their positions are interchanged at a rate faster than ~ 40 MHz. The spacing of the resultant triplet is ~ 20 G. The computed pattern of Figure 10c is very close to the overall triplet pattern observed from the anions of 3,3-dimethyloxetane (Figure 4).

The hyperfine coupling tensor of a β proton of an alkyl radical is also well understood; it is essentially isotropic and is given by the dihedral angle θ of the $\text{C}_\beta\text{-H}_\beta$ bond relative to the p_x orbital.¹⁴

$$A(\text{H}_\beta) = B_0 + B \cos^2 \theta \quad (3)$$

It has been empirically determined that $B_0 = 4$ G, and $B = 50$ G. Thus the two β protons would generally have different coupling constants unless the conformation is such that the two protons have the same dihedral angles.

As stated earlier the ESR spectrum of the anions of trimethylene oxide formed immediately after the first irradiation (Figure 3a) has a quintet pattern of the binomial intensity ratio

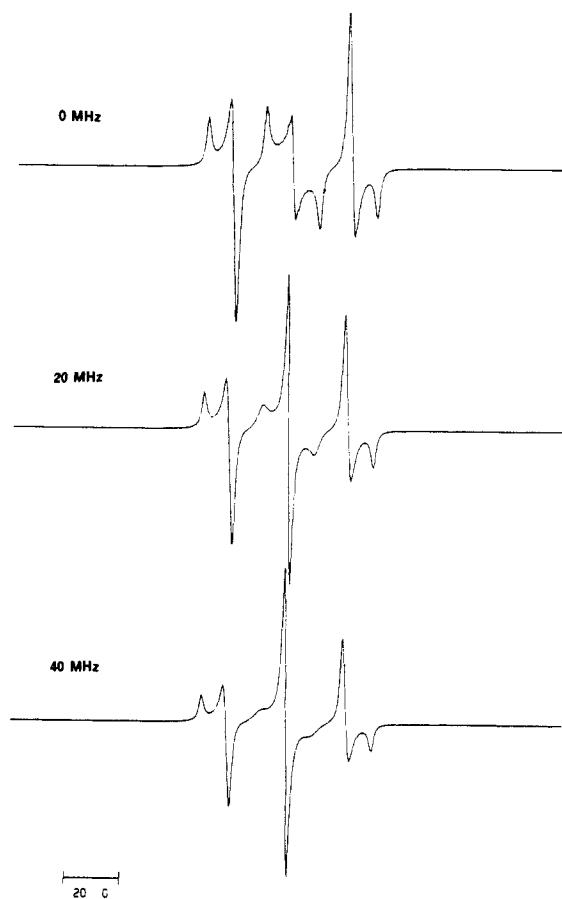


Figure 10. ESR powder patterns of an alkyl radical, RCH_2^\bullet , simulated based on an isotropic g tensor, the model α proton coupling tensor, the $\text{H}_\alpha\text{-C}_\alpha\text{-H}_\alpha$ angle of 120° , and an interchange of the α protons at the rate of 0, 20, and 40 MHz.

expected from the hyperfine interaction of equal magnitude with four protons. The spacings between successive components are ~ 17 G. It follows that the two α protons must be interchanging their positions rapidly and that two β protons have the same dihedral angles. As the β carbon is sp^3 hybridized, the dihedral angles of the two β protons, if equal, must be either 30° or 60° . The former, according to eq 3, predicts the β proton coupling constant of 42 G, while the latter predicts 17 G. Figure 11a shows the spectrum of the trimethylene oxide anion, **2**, simulated based on two α protons interchanging at the rate of 300 MHz, and two β protons having isotropic coupling constants of 17 G. The agreement between the observed (Figure 3a) and simulated spectrum is reasonable. A much better agreement was obtained, however, when the magnitude of the α proton coupling tensor was reduced by 20% (Figure 11b). We believe the conformation revealed here reflects the structure of the anion requiring the least possible rearrangement from the original cyclic form. The O-C-C skeletal chain would thus be nearly planar, the $\text{H}_\alpha\text{-C}_\alpha\text{-H}_\alpha$ sector would be perpendicular to the skeletal plane, and the two β protons would remain in the vicinity of the original positions thus defining dihedral angles of 60° with the resulting semifilled p_x orbital. The indicated reduction of the unpaired electron density at the α carbon suggests that the planar form is retained by a weak σ bonding interaction between the α carbon and the oxygen atom. The unpaired electron would then be in the antibonding orbital of that sector.

As stated earlier, the photoinduced spectral change from the quintet discussed above to the doublet-of-doublet-of-triplet (Figure 3b) is ascribed to a conformational change. The final conformation must be that of lower energy but requiring greater rearrangement. The O-C-C skeletal chain should thus be in either the gauche or trans form. The triplet part of the spectrum in Figure 3b is clearly that arising from the rapidly interchanging α protons. The doublet-of-doublet section with the respective spacings of 46 and

(10) McConnell, H. M.; Strathdee, J. *Mol. Phys.* **1959**, *2*, 129.

(11) Kasai, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 5950.

(12) See, for example: Martin, M. L.; Martin, G. J.; Delpuech, J. *Practical NMR Spectroscopy*; Heyden: London, 1980; pp 293-311.

(13) An example of the modified Bloch equation method applied to an ESR powder pattern is given by the following: Schlick, S.; Kevan, L. *J. Am. Chem. Soc.* **1980**, *102*, 4622.

(14) Morton, J. R. *Chem. Rev.* **1964**, *64*, 453.

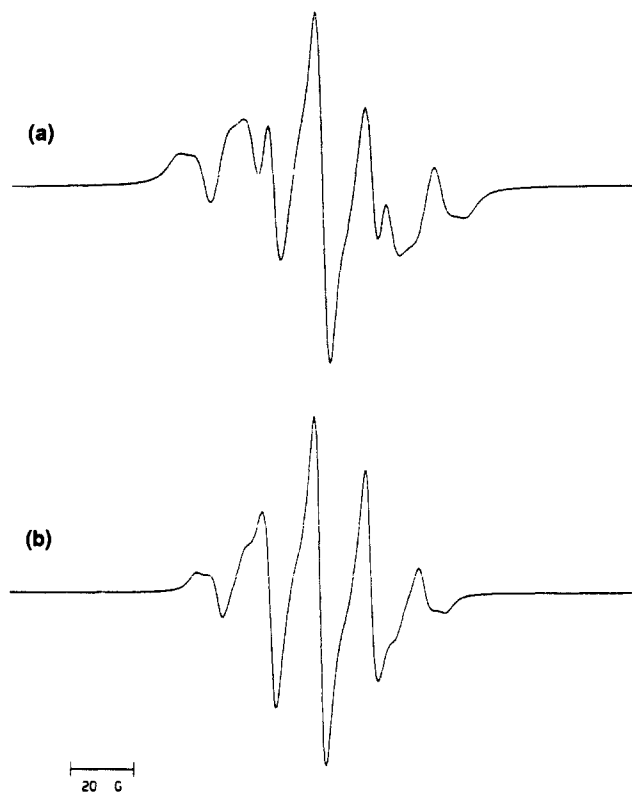


Figure 11. (a) Simulated ESR spectrum of trimethylene oxide anion of the initial conformation based on two α protons interchanging at 300 MHz and isotropic coupling constants of 17 G for the two β protons. (b) Same as (a) except that the α proton coupling tensor had been reduced by 20%.

22 G in Figure 3b is hence ascribed to the β protons. That the two β protons are clearly inequivalent suggests that the O-C-C skeletal chain is in the gauche conformation. The β proton coupling constant of 46 G implies, from eq 3, the dihedral angle of $\pm 24^\circ$ and consequently the dihedral angle of the second β proton of 96° or 144° . These angles in turn predict the coupling constant of 5 or 37 G, neither of which is close to the observed coupling constant of the second β proton. The average of these values, however, is very close to the observed value. What is strongly suggested here is a rapid reorientation of the α CH₂ plane about the C _{α} -C _{β} bond such that the dihedral angle of one of the β protons oscillates between $\pm 24^\circ$.

Figure 12a is a simulated spectrum of O⁻-CH₂-CH₂-CH₂[•] based on a model of rapidly interchanging α protons (at 300 MHz) and the two β protons having a stationary conformation with the respective dihedral angles of -24° and 96° or $+24^\circ$ and 144° with equal probability. Figure 12b is the spectrum of the same radical simulated assuming the rapid reorientation of the α CH₂ plane of $\pm 24^\circ$ described above at the rate of 300 MHz. A simpler pattern results here as each pair of signals correlated through the reorientation in Figure 12a coalesce into a broad singlet. The spacings of the coalesced signals are in good agreement with the observed spacings (Figure 3b). However, in the simulated spectrum, the inner members of the four most prominent signals are as strong as the outer members, while, in the observed spectrum, they are weaker and broader. Due to the symmetry of the postulated oscillation from -24° to $+24^\circ$, the spacings within pairs of signals destined to coalesce in Figure 12a are the same for all the correlated pairs. It can be readily shown that, if the oscillation were not symmetric, all the spacings between the correlated signals would not be the same, and the signals separated further apart would not coalesce as effectively as those with smaller separation. Figure 12c shows the spectrum of the same radical simulated assuming reorientation of the α CH₂ plane of the same amplitude and frequency ($\pm 24^\circ$ at 300 MHz) but with its center of oscillation shifted 3° from the symmetric situation (hence the oscillation from -21° to $+27^\circ$).¹⁵ The spectrum so simulated

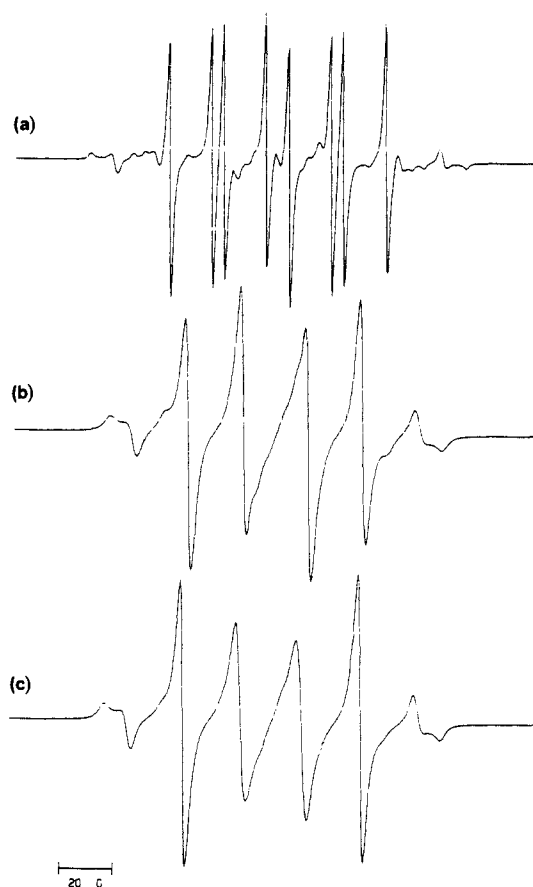


Figure 12. (a) ESR spectrum of trimethylene oxide anion of the second conformation, simulated based on the model coupling tensor of α protons interchanging at 300 MHz, and the β protons having the dihedral angles of either -24° and 96° or 24° and 144° with equal probability. (b) Same as (a) except that the α CH₂ plane was assumed to oscillate $\pm 24^\circ$ at 300 MHz about the C _{α} -C _{β} bond. (c) Same as (b) except the center of the α CH₂ plane oscillation shifted by 3° (see text for detail).

is in excellent agreement with the observed. The sensitivity of the spectrum to small changes in various conformational aspects is intriguing. The numerical values deduced here should be viewed with due cautions as they are subject to uncertainties of B_0 and B in eq 3 and the assumed H _{β} -C _{β} -H _{β} angle. Similar rapid interchange of the α protons and reorientation of the α CH₂ plane by $\pm 30^\circ$ had been concluded for *n*-propyl radicals generated in argon matrix by Adrian et al.¹⁶

As stated earlier, the spectrum of ring-opened ethylene oxide anion has a triplet-of-triplet pattern (Figure 6). The smaller triplet, though recognized only for the outermost components, has spacings of ~ 20 G and has a pattern that is clearly due to interchanging α protons. The larger triplet pattern has spacings of 43 G consistent with the β protons having the dihedral angles of 30° . The central signals of the larger triplet, however, clearly lacks the prominence, had the two β protons been truly equivalent. The central signals of the smaller triplets also appear to lack some prominence. Figure 13a shows the simulated spectrum of ethylene oxide anion based on the model of rapidly interchanging α protons (at 300 MHz) and the two β protons having a fixed dihedral angle of 30° . Figure 13b is the simulated spectrum based on a model of the α protons interchanging at somewhat slower rate (60 MHz) and the α CH₂ plane reorienting at 30 MHz between the orientations deviating $\pm 3^\circ$ from the plane bisecting the H _{β} -C _{β} -H _{β} angle. The agreement between the observed and simulated spectra is considered reasonable.

(15) These angles may be obtained analytically from equations $B_0 + (B/2)[\cos^2 \alpha + \cos^2 \beta] = 46$ G and $B_0 + (B/2)[\cos^2(\alpha + 120) + \cos^2(\beta + 120)] = 22$ G.

(16) Adrian, F. J.; Cochran, E. L.; Bowers, V. A. *J. Chem. Phys.* **1973**, *59*, 3946.

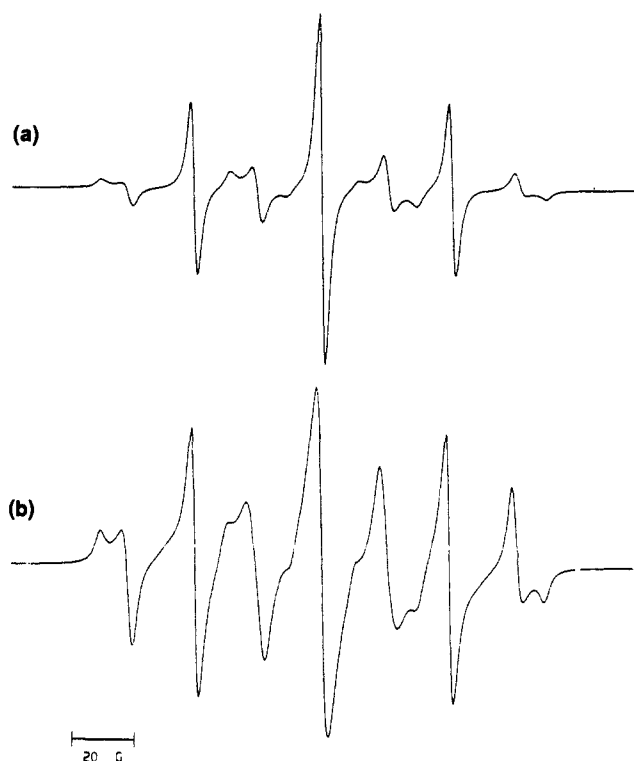


Figure 13. (a) Simulated ESR spectrum of ethylene oxide anion based on the model coupling tensor of the α protons interchanging at 300 MHz and the β protons having fixed dihedral angles of 30° . (b) Same as (a) except that a slower rate of α proton interchange at 60 MHz and oscillation of the α CH_2 plane at 30 MHz between the orientations deviating $\pm 3^\circ$ from the plane bisecting the $\text{H}_\beta\text{-C}_\beta\text{-H}_\beta$ angle were assumed.

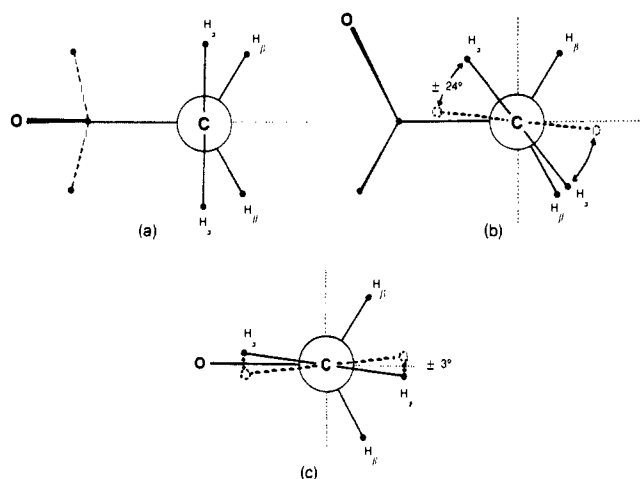


Figure 14. (a and b) Conformations of the ring-opened trimethylene oxide anion before and after photoisomerization. (c) Conformation of ring-opened ethylene oxide anion.

The two conformations of the ring-ruptured trimethylene oxide anion and that of the ring-ruptured ethylene oxide anion delineated above are shown in the Newman diagram in Figure 14. For the trimethylene oxide anion of the gauche form (Figure 14b), if one assumes the normal structural parameters, the dihedral angle of the line connecting the α carbon and the oxygen atom relative to the horizontal axis is $\sim 29^\circ$, and the reorientation of the α CH_2 plane concluded above is consistent with the reorientation of the plane about this line. The slower rate of interchange of the α

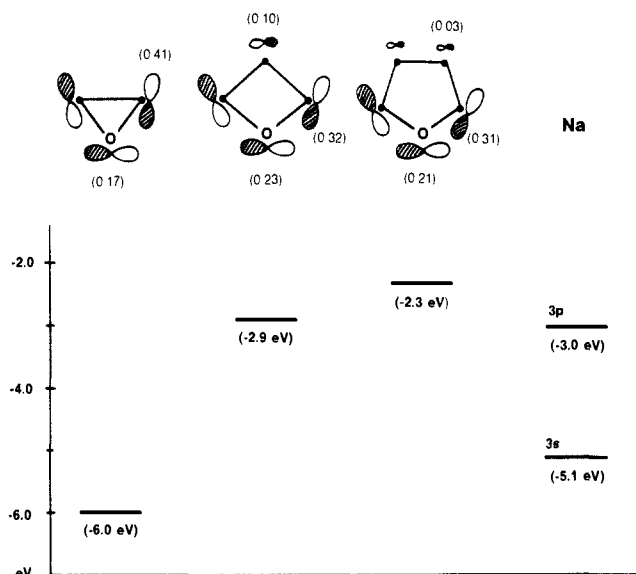


Figure 15. LUMO's (lowest unoccupied molecular orbital) of ethylene oxide, trimethylene oxide, and tetrahydrofuran given by EHT calculations. The fractional compositions in terms of the relevant atomic p orbitals and the energy levels of LUMO's of the neutral molecules are depicted.

protons in the ethylene oxide anion may be ascribed to a possible hydrogen bonding.

The facility with which the electron transfer occurred for ethylene oxide indicates an unusually strong electron affinity of this molecule. Shown schematically in Figure 15 are the LUMO's (lowest unoccupied molecular orbital) and their energy levels of ethylene oxide,¹⁷ trimethylene oxide,⁹ and tetrahydrofuran¹⁸ given by EHT calculations. The energy levels of the Na 3s and 3p atomic orbitals are also shown.¹⁹ In every epoxy system examined here the LUMO is an antibonding in-plane σ orbital. And even for trimethylene oxide and tetrahydrofuran, it is rather confined to the C-O-C sector. It is particularly revealing that the energy level of the LUMO of ethylene oxide is exceptionally low and is, in fact, lower than the Na 3s level. It must be that the (ethylene oxide)₁Na⁰ complex is observed as the spontaneous electron transfer from the Na sp orbital to the ethylene oxide LUMO is symmetry forbidden. Such symmetry barrier no longer exists when the second ligand approaches the monoligand complex. The absence of (ethylene oxide)_{2,3}Na⁰ complexes and the presence of ethylene oxide anions without photoirradiation in the Na/ethylene oxide/Ar system are thus accounted for.

The MO calculations also showed that the C-O bond strengths (as given by the reduced overlap populations²⁰) are 0.43, 0.48, and 0.53 for ethylene oxide, trimethylene oxide, and tetrahydrofuran, respectively. The configurational strain in ethylene oxide is responsible not only for the weaker C-O bond but also for the formation of less antibonding, hence lower lying LUMO.

The present study clearly demonstrated the extra sensitivity of the ethylene oxide moiety toward dissociative electron capture. The high sensitivity of epoxytated (meth)acrylate polymers as electron beam negative resist can surely be accounted for by such a process. The study also showed that incorporation of trimethylene oxide moiety should also increase the electron beam sensitivity of these polymers.

(17) Cunningham, G. L., Jr.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D. *J. Chem. Phys.* **1951**, *19*, 676.

(18) Geise, H. J.; Adams, W. J.; Bartell, L. S. *Tetrahedron* **1969**, *25*, 3045.

(19) Moore, C. E. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1971**, 35.

(20) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489.