Succinimidyl and Phthalimidyl Radicals: Matrix Isolation ESR Study

Paul H. Kasai

*Contribution from IBM Almaden Research Center, San Jose, California 95120.
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Abstract: Succinimidyl radical, phthalimidyl radical, and 1,8-naphthalimidyl radical were generated in argon matrices by cocondensation of Na atoms and corresponding imide triflates at near liquid helium temperature. Spontaneous Na atom-to-triflate electron transfer occurred, and the resulting anions spontaneously dissociated to yield imidyl radicals and triflate anions. In the case of succinimidyl triflate, the observed ESR spectrum was determined as that of β-(isocyanatocarbonyl)ethyl radicals resulting from ring-opening of the succinimidyl radical. In the cases of phthalimidyl triflate and 1,8-naphthalimidyl triflate, the ESR spectra due to the "nitrogen centered" imidyl radicals were observed. The ^{14}N hyperfine coupling tensors determined for these radicals unambiguously revealed their π radical ground state. When the matrix containing the phthalimidyl radical was exposed to mild radiation ($\lambda = 600 \pm 50$ nm), the ESR spectrum changed to that of an ortho-substituted phenyl radical consistent with its ring-opening process. 1,8-Naphthalimidyl radical did not undergo the corresponding ring-opening process when treated similarly.

Introduction

The electronic ground state of the succinimidyl radical has long eluded a definitive characterization. The basic issue had been whether the radical was a σ radical **1**, the unpaired electron of


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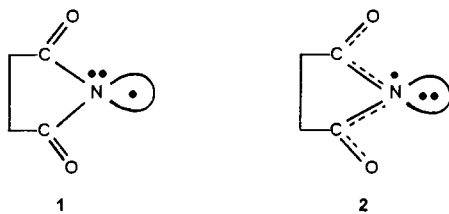
which was localized essentially in a nitrogen σ orbital, or was a π radical **2** where the unpaired electron would be in the π orbital delocalized over the O–C–N–C–O sector.[1,2]

Skell and co-workers reported evidences for the involvement of both the σ and π succinimidyl radicals in reactions of *N*-halogenosuccinimides, and concluded that the ground state was the π state but succinimidyl radicals in the readily accessible σ state were much more reactive. They estimated an upper limit of ~75 KJ mol^{-1} for the π–σ separation from their experimental results.[3]

Many theoretical investigations on the σ versus π issue of the succinimidyl radical have been performed at various levels of sophistication.[4-8] They all predicted the π radical ground state. A more recent study using "state-of-the-art" ab initio MO technique revealed an extreme sensitivity of the problem both to basis set size and to the degree of electron correlation, and placed, after large scale CI calculations, the σ level at ~21.5 kJ mol^{-1} above the π radical ground state.[8]

The rearrangement of *N*-bromosuccinimide to 3-bromopropanoyl isocyanate discovered many years ago is attributed to thermally induced ring-opening of the succinimidyl radical to form the β-(isocyanatocarbonyl)ethyl radical (Scheme I).[9,10] The

Scheme I

1   3
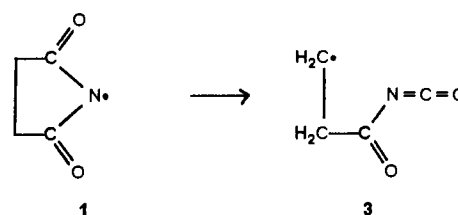
symmetry consideration dictates that the ring-opening process occurs from the (excited) σ radical state.[4,7]

The ESR spectrum of the succinimidyl radical in solution has never been observed. That the succinimidyl radical is generated during the photolytic decomposition of *N*-bromosuccinimide is shown by the ESR spin trapping technique.[11-13] This method, however, does not yield a clue regarding the electronic state of the radical being trapped. An attempt to generate the succinimidyl radical by X-ray irradiation of *N*-chlorosuccinimide at low temperature failed.[14] Lund and co-workers succeeded in detecting the ESR spectrum of the succinimidyl radical in single crystals of succinimide X-ray irradiated at 26 K.[15] Based on the anisotropy of the ^{14}N hyperfine coupling (hfc) tensor, they concluded that the radical was in the π state. The spectrum was observed only from crystals grown from water, but not from crystals grown in ketone.

The technique of generating and entrapping (reactive) neutral radicals in rare gas matrices via a dissociative electron capture process was reported many years ago.[16] The technique consists of cocondensing Na atoms and molecules RX (where X is an electrophilic leaving unit) in an argon matrix, and effecting an electron transfer between them with mild radiation ($\lambda = 590$ nm).

$$Na + RX \xrightarrow{h\nu} Na^+ + R^\bullet + X^-$$

Generally the resulting neutral radicals are not affected by the continuing photoirradiation. For imidyl radicals, however, this turns out not to be the case, as will be shown later.

Recently we have observed that, when the leaving unit is a triflate (trifluoromethanesulfonate, $CF_3–SO_2–O^-$), its electron affinity is such that both the Na-to-RX electron transfer and the

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subsequent dissociation occur spontaneously during collision in space (as the two beams merge near the cold finger) or in the fluid surface layer of the matrix during deposition.[17] Photoirradiation is hence not required. We report here results of an ESR study of succinimidyl, phthalimidyl, and 1,8-naphthalimidyl radicals generated in argon matrices from the corresponding imidyl triflates by this spontaneous dissociative electron capture process. For comparison, matrices containing Na atoms and, respectively, N-chlorosuccinimide and N-chlorophthalimide were also prepared and examined; here photoirradiation was needed to induce the electron transfer.

In the case of succinimidyl triflate, the observed ESR spectrum was determined as that of β-(isocyanatocarbonyl)ethyl radical resulting from ring-opening of the succinimidyl radical. In the cases of phthalimidyl and 1,8-naphthalimidyl triflates, the ESR spectra due to the "nitrogen centered" imidyl radicals were observed. The ^{14}N hfc tensors determined for these radicals unambiguously revealed their π radical ground state. When the matrix containing the phthalimidyl radical was exposed to mild radiation ($\lambda = 600 \pm 50$ nm), the ESR spectrum changed to that of an ortho-substituted phenyl radical consistent with its ring-opening process. The 1,8-naphthalimidyl radical did not show the corresponding ring-opening process when treated similarly.

Experimental Section

The liquid helium cryostat–ESR spectrometer system that would enable trapping of vaporized metal atoms in inert gas matrices and examination of the resulting matrices by ESR have been described earlier.[16] The technique of trapping Na atoms as electron donors and molecules of interest as acceptors and inducing electron transfer between them by mild radiation ($\lambda = 590$ nm, corresponding to the Na 3s → 3p transition) has also been described.[16] The cations and product(s) of electron capture thus generated are effectively isolated in the matrix. In the present series of experiments, the Na atoms were generated from a resistively heated stainless steel tube (250 °C), and acceptor molecules of choice (imidyl halides and triflates) were sublimed from a Pyrex reservoir independently heated to 100 ~ 150 °C.

N-Chlorosuccinimide and N-chlorophthalimide were obtained from Aldrich Chemical Co. and Tokyo Kasei Ind., respectively, and were purified by sublimation prior to deposition. Succinimidyl triflate, phthalimidyl triflate, and 1,8-naphthalimidyl triflate were kindly supplied by N. P. Hacker, and R. A. DiPietro of IBM Almaden Research Center.

The ESR spectrometer used was an X-band spectrometer (IBM Instruments Model 200D), and the microwave frequency locked to the sample cavity was typically 9.42 GHz. All the spectra were obtained while the matrix was maintained at 4 K. For photoirradiation of the matrix, a high pressure Xe–Hg lamp (Oriel, 1 kW unit) was used. The light beam was passed through a water filter and a broad band interference filter of choice, and was focused on the cold finger ~40 cm away.

Spectra and Assignments

Succinimidyl Radicals. An argon matrix in which Na atoms and succinimidyl triflate molecules had been cocondensed showed an ESR spectrum comprising a widely spaced quartet due to unreacted Na atoms,[18] and a multiplet spread over ±100 G centered about the position of **g** = 2.00. No splitting pattern attributable to the ^{14}N hyperfine interaction was discerned in the multiplet. In order to ascertain the relevance of the multiplet to the succinimidyl radical, an argon matrix containing Na atoms and N-chlorosuccinimide was prepared. The latter matrix as prepared showed only the ESR signals due to Na atoms. When the matrix was irradiated with yellow light ($\lambda = 600 \pm 50$ nm) for 8 min, the Na signals disappeared completely, and an intense multiplet appeared centered about the position of **g** = 2.00. The multiplet was identical, in its pattern, with that observed from the Na/succinimidyl triflate matrix; its intensity was much stronger, reflecting the completeness of the process. The multiplet observed from the Na/N-chlorosuccinimide matrix is shown in Figure 1a. In order to better gauge the relative intensity of individual components, the multiplet is shown integrated in Figure 1b. We envisaged that the multiplet seen here was that of the
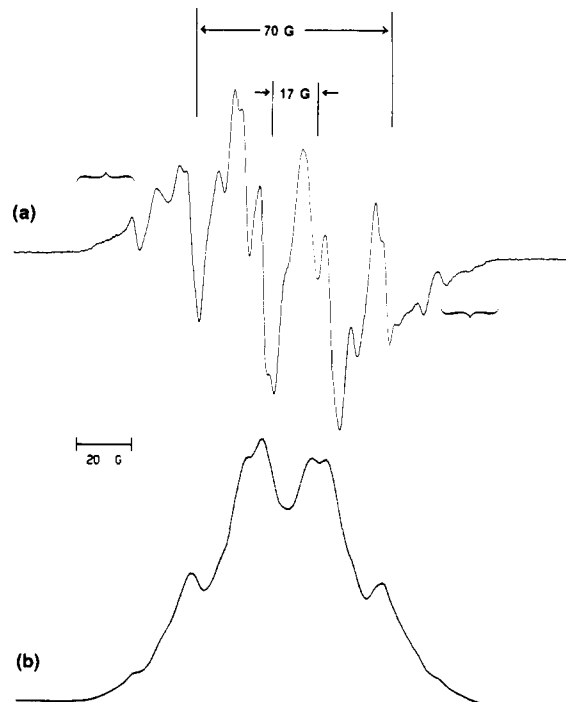
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Figure 1. (a) ESR spectrum of β-(isocyanatocarbonyl)ethyl radicals observed from the Na/N-chlorosuccinimide/Ar system after photoirradiation ($\lambda = 600 \pm 50$ nm). (b) Above spectrum integrated.
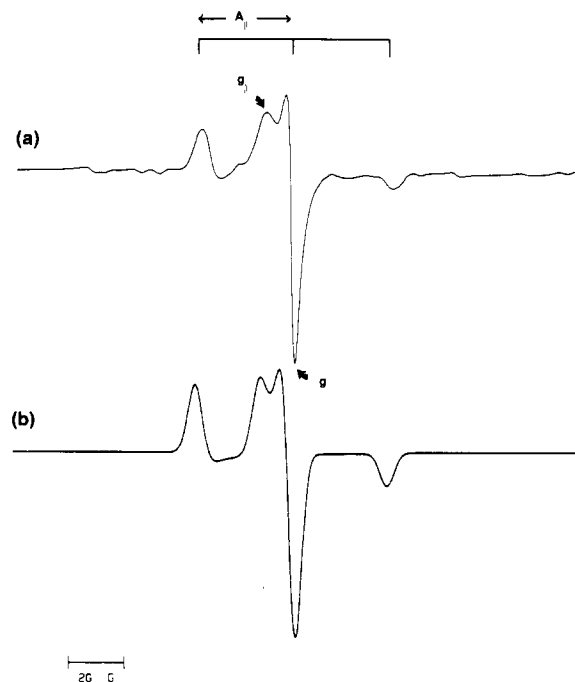

Figure 2. (a) ESR spectrum of phthalimidyl radicals observed from the Na/phthalimidyl triflate/Ar system. (b) ESR spectrum simulated based on the parameter given in the text.

β-(isocyanatocarbonyl)ethyl radical, **3**, and that the anticipated spontaneous electron transfer indeed occurred in the Na/succinimidyl triflate case. The complex splitting pattern is due to the hyperfine interactions with the two α and two β protons which are in turn modulated by torsional oscillation of the α C–H$_2$ plane. More detailed analysis and substantiation of the assignment are presented in the Discussion.

Phthalimidyl Radicals. When examined as prepared, an argon matrix in which Na atoms and phthalimidyl triflate molecules had been cocondensed showed, in addition to the signals due to unreacted Na atoms, a rather simple but highly anisotropic ESR spectrum centered about the position of **g** = 2.00 (Figure 2a). The
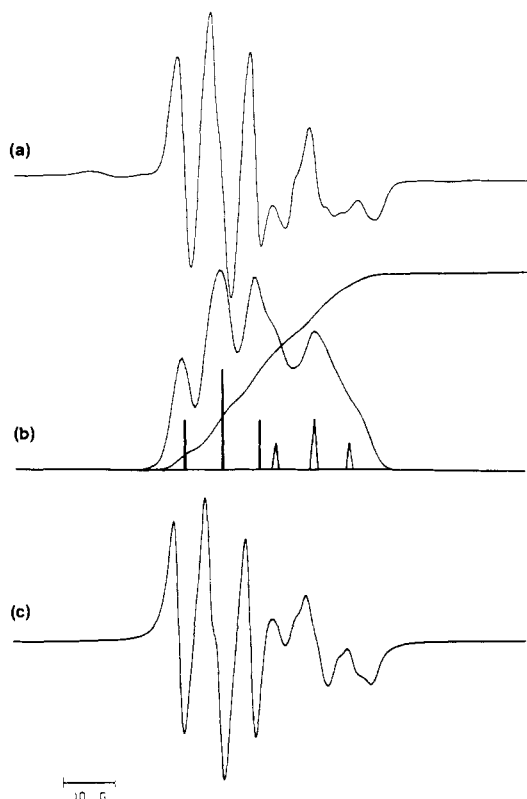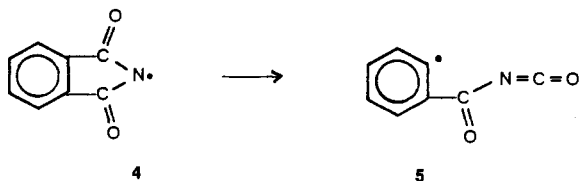
Figure 3. (a) ESR spectrum of the Na/phthalimidyl triflate/Ar system observed after photoirradiation ($\lambda = 600 \pm 50$ nm, 8 min). (b) Integral and double-integral of spectrum a. (c) ESR spectrum of ortho-substituted phenyl radicals based on the parameters given in the text.

Scheme II

spectrum is characterized by a pair of signals of same form but of opposite signs, displaced symmetrically from the intense central component. The pattern is exactly that expected from a ^{14}N ($I = 1$) hfc tensor of the form $A_\parallel \gg A_\perp \cong 0$.[19] This particular form of a ^{14}N hfc tensor is encountered whenever the semioccupied orbital (SOMO) of the radical involves, in an LCAO description, only the 2p valence orbital of the nitrogen atom, and not its 2s orbital. The ^{14}N hfc tensors of $CH_2 = N^\bullet$ and NF_2 radicals are exemplary.[20,21] The spectrum is hence assigned to the phthalimidyl radical in the π ground state.

Most interestingly, when the matrix showing the ESR spectrum of phthalimidyl radicals was subsequently irradiated with yellow light ($\lambda = 600 \pm 50$ nm), the spectrum changed completely to that shown in Figure 3a. The integrated and double-integrated forms of the same spectrum are shown in Figure 3b. The photoconverted spectrum was thus recognized as a severely skewed doublet of 1:2:1 triplets as indicated. It was hence assigned to the ortho-substituted phenyl radical, **5**, resulting from ring-opening of the phthalimidyl radical, **4** (Scheme II). The doublet splitting of ~18 G is attributed to the ortho proton, and the triplet pattern with successive spacings of ~7 G to the two meta protons. The

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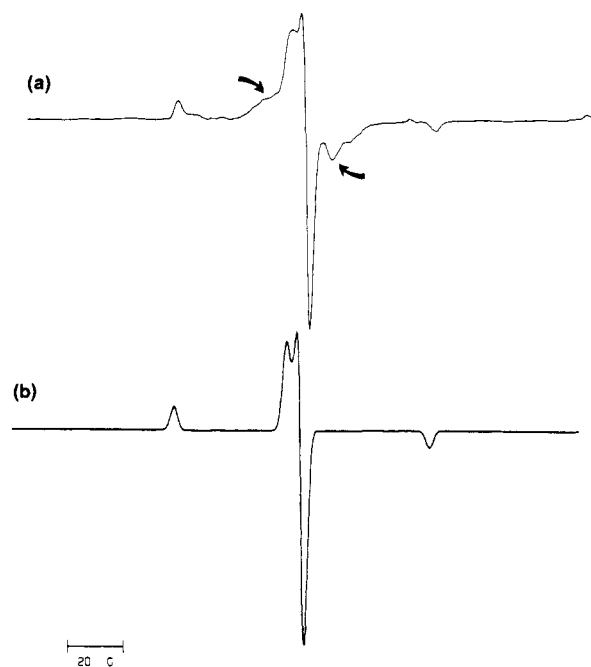(21) Kasai, P. H.; Whipple, E. W. *Mol. Phys.* **1965**, *9*, 497.

Figure 4. (a) ESR spectrum of 1,8-naphthalimidyl radicals observed from the Na/1,8-naphthalimidyl triflate/Ar system. (b) ESR spectrum simulated based on the parameter given in the text.

severe skewness is ascribed to a large anisotropy of the ortho-proton hfc tensor and the g-tensor anisotropy.

In order to gain further substantiation of the envisaged process, an argon matrix containing Na atoms and *N*-chlorophthalimide was prepared. The matrix as prepared showed only the ESR signals due to Na atoms. Irradiation of the matrix with yellow light ($\lambda = 600 \pm 50$ nm) resulted in total disappearance of the Na signals and appearance of the spectrum due to the ortho-substituted phenyl radical, **5**, as expected. Detailed analyses of the ESR spectra of both radicals **4** and **5** are presented in the Discussion.

1,8-Naphthalimidyl Radicals. When examined as prepared, an argon matrix in which Na atoms and 1,8-naphthalimidyl triflate molecules had been cocondensed showed the ESR signals due to isolated Na atoms and a weak signals indicating the ^{14}N hfc interaction characteristic of a nitrogen centered radical. Upon irradiation with yellow light ($\lambda = 600 \pm 50$ nm) for 8 min, the signals due to Na atoms disappeared and that of the nitrogen centered radical intensified ($\sim\times 10$). The latter pattern observed after photoirradiation is shown in Figure 4a.

The broad shoulders indicated by arrows in Figure 4a are believed to be due to thermal decomposition product(s) inadvertently formed during the deposition (sublimation) process. Their intensities relative to the major pattern increased with increasing temperature of sublimation. The axial asymmetry of the ^{14}N hfc tensor ($A_\parallel \gg A_\perp \cong 0$) recognized for the major pattern is very similar to that observed from the phthalimidyl radical, **4**; the magnitude of $A_\parallel$ is substantially larger, however. The major pattern seen here is thus assigned to the 1,8-naphthalimidyl radical, **6**, having the π ground state. Significantly, unlike the phthal-

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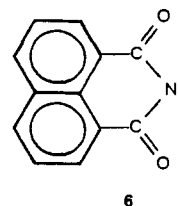
imidyl radical **4**, the 1,8-naphthalimidyl radical is photostable. The ESR spectrum of the matrix remained unchanged even after irradiation with UV light ($\lambda = 325 \pm 50$ nm) for 20 min. Detailed analysis of the spectrum is presented in the Discussions.
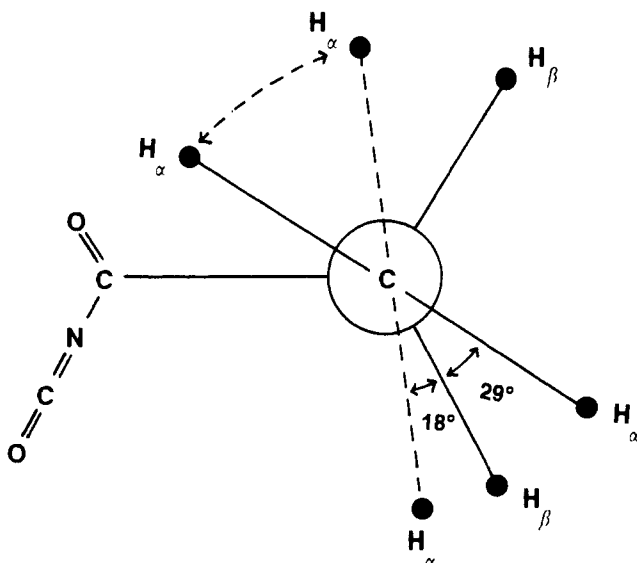
Figure 5. Newman diagram of β-(isocyanatocarbonyl)ethyl radicals of the two limiting orientations of the α-CH_2 plane.

Discussion

β-(**Isocyanatocarbonyl)ethyl Radical.** The β-(isocyanato-carbonyl)ethyl radical, **3**, is a β-substituted ethyl radical, the ESR spectrum of which is determined essentially by the hfc interactions with the two α protons and the two β protons. The hfc tensors of α and β protons of an alkyl radical are well understood. The hfc tensor of an α proton is rather anisotropic and may be given as follows:[22,23]

$$A_{\parallel} = 12 \text{ G} \qquad A_{\perp\parallel} = 22 \text{ G} \qquad A_{\perp\perp} = 35 \text{ G}$$

Here, $A_{\parallel}$ is the diagonal element of the tensor in the direction parallel to the C–H bond, and $A_{\perp\parallel}$, for example, is the diagonal element perpendicular to the C–H bond but parallel to the p_π orbital of the α carbon. Thus, for a primary radical such as **3**, the orientations of the hfc tensors of the two α protons differ from each other by $\sim120°$ about the p_π orbital, and the triplet pattern with a prominent central component would not result unless the two protons exchange their positions rapidly (>40 MHz).[24,25] The hfc tensor of a β proton is essentially isotropic and is determined by the dihedral angle θ of the C_β–H_β bond relative to the p_π orbital of the α carbon.[26]

$$A(H_\beta) = B_0 + B \cos^2 \theta \tag{1}$$

It has been empirically determined that $B_0 = 4$ G and $B = 50$ G. Thus, as the dihedral angles of the two β protons differ by $\sim120°$, their hfc constants would generally be different.

In the ESR spectrum seen in Figure 1a, the weak, broad components indicated at the extreme ends of the pattern have the shapes characteristic of the outer components of the triplet due to rapidly exchanging α protons.[24,25] The major components discernible between these signals must then reflect the splittings of the central component of the α proton triplet by the two β protons. The largest and the smallest spacings between these prominent peaks indicated respectively in the figure must then be equal to $A(H_\beta)_1 + A(H_\beta)_2$ and $A(H_\beta)_1 - A(H_\beta)_2$, respectively, where $A(H_\beta)_1$ and $A(H_\beta)_2$ are the coupling constants of the two β protons given by eq 1. The former spacing is 70 G and the latter is 17 G. As stated earlier, the dihedral angles of the two β protons differ by $\sim120°$, and no one particular conformation would yield the β proton coupling constants consistent with these deductions.
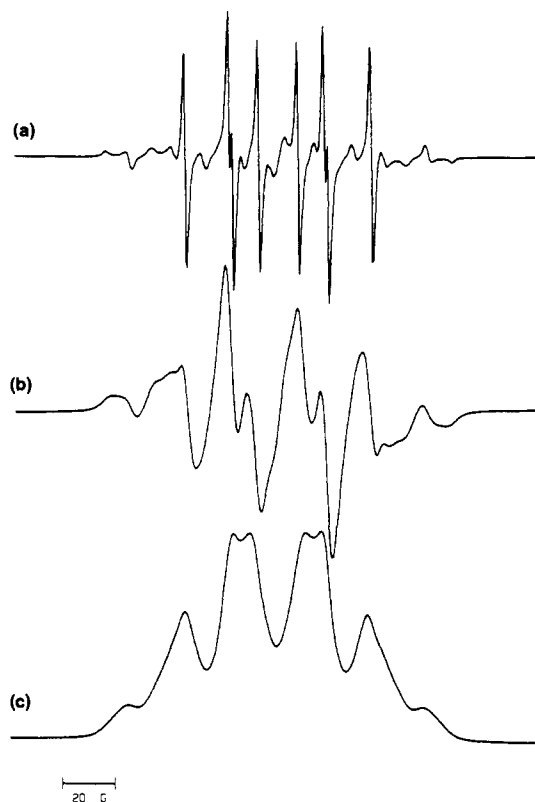

Figure 6. (a) ESR spectrum of β-(isocyanatocarbonyl)ethyl radicals simulated based on the model α- and β-proton hfc tensors and assuming static, equimolar mixture of radicals of the two limiting conformations given in Figure 5. (b) ESR spectrum of the above system simulated allowing exchange of the two conformations at 60 MHz. (c) Integral of spectrum b.

The ESR spectrum of n-propyl radicals isolated in an argon matrix had been studied by Adrian et al.[27] Recently we reported on the ESR spectrum of trimethylene oxide anion of the ring-ruptured form, O^-–CH_2–CH_2–$CH_2^{\bullet}$, generated in an argon matrix.[25] In both cases it was found that the α-CH_2 plane oscillated between two angular positions about the C_α–C_β bond and the observed spectra were those resulting from rapid exchange between the two spectra of the limiting conformations. We surmised that the extra complexity observed in the present case was due to similar but much slower oscillation of the α-CH_2 plane. The conformation with the β proton dihedral angles of $\theta_1 = -1°$ and $\theta_2 = +119°$ would give $A(H_\beta)_1 + A(H_\beta)_2 = 70$ G, and the conformation of $\theta_1 = -48°$ and $\theta_2 = +72°$ would give $A(H_\beta)_1 - A(H_\beta)_2 = 17$ G. The Newman diagram of the radical with these limiting conformations is shown in Figure 5.

Figure 6a shows the ESR spectrum of radicals **3** simulated based on (1) the model α proton coupling tensor given above and the exchange of the α protons at 300 MHz, and (2) the β proton coupling constants given by eq 1 for the static situation, i.e., an equimolar mixture of the radicals having one or the other of the two limiting conformations discussed above (see also Figure 5). Figure 6b is the spectrum of the same system simulated including the effect of the oscillation of the α-CH_2 plane between the two limiting orientations at 60 MHz.[28] Figure 6c is its integrated form. The agreement between the observed (Figure 1, a and b) and the simulated (Figure 6, b and c) is considered reasonable in view of uncertainties related to eq 1 and total neglect of the anisotropies of the β proton coupling tensors and the g tensor. It is thus shown that the α-CH_2 plane of radical **3** is oscillating with

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(27) Adrian, F. J.; Cochran, E. L.; Bowers, V. A. *J. Chem. Phys.* **1973**, *59*, 3946.
(28) A usual ESR powder pattern program (ref 23) was modified to include the effect of exchanging protons by the method of modified Bloch equation.

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the amplitude of $\pm 23.5°$ and the frequency of 60 MHz. The corresponding values determined for the trimethylene oxide anion of the ring-ruptured form (O^-–CH_2–CH_2–CH_2·) are $\pm 24°$ at 300 MHz.[25] For the n-propyl radical, Adrian et al. concluded a rapid oscillation of the α-CH_2 plane of $\pm 30°$.[27] The slower oscillation of the α-CH_2 plane in radical **3** implicates a proximity of the isocyanato end-group to the radical terminus.

Phthalimidyl Radical. As stated earlier the ESR spectrum of the phthalimidyl radicals (Figure 2a) is dominated by the ^{14}N hfc tensor of the form $A_{\parallel} \gg A_{\perp} \simeq 0$, and is hence assigned to the radical in the π ground state. The observed splittings yield the following ^{14}N hfc tensor:

$$A_{\parallel} = 95 \pm 3 \text{ MHz} \qquad A_{\perp} = 0 \pm 3 \text{ MHz}$$

It has been shown that, when the distribution of the unpaired electron in the vicinity of a magnetic nucleus is axially symmetric, the hfc tensor of the nucleus may be given as follows:[29]

$$A_{\parallel} = A_{iso} + 2A_{dip} \qquad A_{\perp} = A_{iso} - A_{dip} \qquad (2)$$

where

$$A_{iso} = g_e\beta_e g_n\beta_n(8\pi/3)|\phi(0)|^2$$

$$A_{dip} = g_e\beta_e g_n\beta_n\left\langle\frac{3\cos^2\alpha - 1}{2r^3}\right\rangle = g_e\beta_e g_n\beta_n\frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle_p$$

Here $|\phi(0)|^2$ represents the spin density at the nucleus, r the distance between the nucleus and the electron, and α the angle between r and the symmetry axis. In an LCAO description of the semioccupied molecular orbital (SOMO), only the spin density in an s orbital contributes to A_{iso}, and those in non-s orbitals contribute to A_{dip}. When SOMO does not contain an s orbital, a small A_{iso} is induced via polarization of filled s orbitals, however. The second expression for A_{dip} is for a unit spin density in a p orbital. The atomic values computed from the Hartree–Fock wave functions for a unit electron density in the nitrogen 2s and 2p atomic orbitals are $A^0_{iso}(2s)_N = 1811$ MHz and $A^0_{dip}(2p)_N = 55.5$ MHz, respectively.[30] Analysis of the observed ^{14}N hfc tensor of the phthalimidyl radical according to eq 2 yields $A_{dip} = A_{iso} = 32$ MHz. A_{dip} of 32 MHz corresponds to the electron density of 58% in the N 2p orbital. A_{iso} of 32 MHz corresponding to the electron density of 1.8% in the N 2s orbital is attributed to the polarization process.

The intense feature at center of the spectrum is mostly due to the $m_I = 0$ component, and the g tensor of the radical can be readily assessed from this sector as indicated. It has been shown that, for a radical with a nondegenerate ground state $|0\rangle$, deviation of the g term from the spin only value $g_e = 2.0023$ is given as follows:[31]

$$g_i - g_e = -2\lambda\sum_n\frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_0} \qquad (3)$$

Here i ($=x, y, z$) represents a principal axis of the g tensor, L_i the orbital angular momentum operator, and λ the one-electron spin–orbit coupling constant. The summation is performed for all the excited states. In evaluating eq 3 in terms of LCAO-MO's, only one-centered integrals may be retained, and for each atomic integral the spin–orbit coupling constant of the particular atom is used. Let us identify the direction perpendicular to the molecular plane of the phthalimidyl radical as the z axis, and the line bisecting its C–N–C angle as the x axis. It follows immediately that, for the phthalimidyl radical in the π state, $g_z - g_e = 0$. Excited states most likely responsible for a significant g shift are those involving the nitrogen lone pair electrons and those of oxygen lone pair electrons. As these electrons are essentially in the p_x orbitals of the respective atoms, a large positive g shift is expected

Table I. Comparison of g_y and A_{dip} of Succinimidyl, Phthalimidyl, and 1,8-Naphthalimidyl Radicals

radical	g_y	A_{dip} $(=A_{iso})$, MHz	$\rho(2p_x)_N$	ref
succinimidyl	2.0143	29	0.52	15
phthalimidyl	2.0093	32	0.57	this work
1,8-naphthalimidyl	2.0059	42	0.76	this work

in the y direction. The g tensor and the ^{14}N hfc tensor of the phthalimidyl radical were thus assigned in the molecular axes as follows:

$$g_x = 2.0023 \qquad A_x = 0 \text{ MHz}$$

$$g_y = 2.0093 \qquad A_y = 0 \text{ MHz}$$

$$g_z = 2.0023 \qquad A_z = 95 \text{ MHz}$$

Figure 2b shows the simulated spectrum of phthalimidyl radicals based on these tensors and a Gaussian line shape with the line width (fwhh) of 6 G.

o-(Isocyanatocarbonyl)phenyl Radical. Figure 3c shows a computer simulated spectrum of an ortho-substituted phenyl radical based on the following parameters:

$$g_x = 2.0034 \qquad g_y = 2.0014 \qquad g_z = 2.0023$$

$$A_x = 17.0 \quad A_y = 24.0 \quad A_z = 19.0 \text{ G (for the ortho proton)}$$

$$A_x = A_y = A_z = 8.0 \text{ G (for one meta proton)}$$

$$A_x = A_y = A_z = 6.0 \text{ G (for the other meta proton)}$$

The simulation was attained by "borrowing" the g tensor and the proton hfc tensors of the phenyl radical determined earlier, and making minor adjustments of the hfc tensors for an improved fit.[32] In the original assignment of the phenyl radical, the tensors for the meta protons were shown to have small anisotropy, and detailed fit was obtained only after the differences in the orientations of the principal axes of all the tensors were considered. The agreement of the spectrum simulated here to the observed (Figure 3a) is hence considered reasonable and sufficient to be construed as an evidence for the postulated process (Scheme II).

1,8-Naphthalimidyl Radical. Analysis of the 1,8-naphthalimidyl radical spectrum following the scheme adopted in the analysis of the phthalimidyl radical is straightforward. Again, identifying the direction perpendicular to the molecular plane as the z axis and the line bisecting the C–N–C angle as the x axis, the g tensor and the ^{14}N hfc tensor were determined as follows:

$$g_x = 2.0023 \qquad A_x = 0 \text{ MHz}$$

$$g_y = 2.0059 \qquad A_y = 0 \text{ MHz}$$

$$g_z = 2.0023 \qquad A_z = 126 \text{ MHz}$$

Figure 4c is the simulated spectrum of 1,8-naphthalimidyl radicals based on these tensors and a Gaussian line shape with line width of 3 G.

Stability of Imidyl Radicals. The propensity of the succinimidyl radical to isomerize to a primary alkyl radical **3** (Scheme I) notwithstanding, different degrees of stability toward the corresponding ring-opening process shown by the phthalimidyl and 1,8-naphthalimidyl radicals are intriguing.

The g_y values (the g value showing the largest deviation from the spin only case) and ^{14}N A_{dip} ($=A_{iso}$) of the phthalimidyl and 1,8-naphthalimidyl radicals determined in the present study are compiled in Table I together with the corresponding values of the succinimidyl radical determined earlier from an irradiated single crystal of succinimide. Also included in the table are the unpaired electron densities in the nitrogen p_x orbital determined from A_{dip}. As stated above, the excited states responsible for the observed

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positive shift in g_y are those involving the nitrogen lone pair electrons and/or those of oxygen lone pair electrons. We note in Table I that the g_y shift is inversely related to the unpaired electron density in the N p_π orbital. Decreasing unpaired electron density in the N p_π orbital indicates increasing importance of the resonance structure π_O in an imidyl radical of the π ground state (see below). It must be that the oxygen lone pair electrons are

$$\pi_N \longleftrightarrow \pi_O \quad \xrightarrow{h\nu} \quad \sigma_O$$
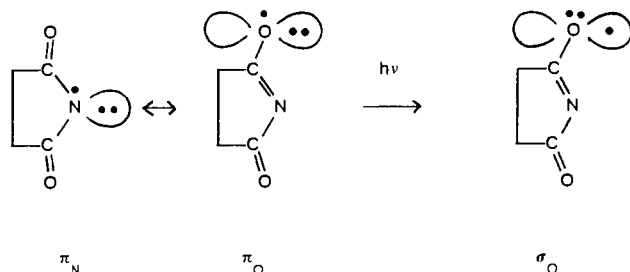
mostly responsible for the observed g_y shift; the spin–orbit coupling constant of oxygen is $\sim$0.01 eV and is three times larger than that of nitrogen.[33]

The facility with which an imidyl radical undergoes the ring-opening process also appears to be inversely related to the unpaired electron density in the N p_π orbital. Possible importance of the (excited) σ_O state in the β scission of succinimidyl radical to form β-(isocyanatocarbonyl)ethyl radical had been pointed out by Koenig and Wielesek,[4] and also by Dewar and Olivella.[7] We suggest that the thermal and/or photo-induced ring-opening of succinimidyl and phthalimidyl radicals observed in the present study involves the $\pi \rightarrow \sigma_O$ transition, and its transition probability increases with increasing contribution of the resonance structure π_O in the π ground state. Succinimidyl radicals detected by Lund, et al.[15] in a single crystal of succinimide irradiated by X-ray at 26 K and maintained at that temperature must have been stabilized by the crystal environment. The radicals in the crystal decayed at $\sim$65 K. More significantly, the radicals were generated only in crystals grown from water and not in crystals grown from ketone. Hydrogen bonding involving the carbonyl oxygen, for example, could impede the ring-opening process involving the σ_O state.

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Heats of Formation of Organic Molecules. 2. The Basis for Calculations Using Either ab Initio or Molecular Mechanics Methods. Alcohols and Ethers

Norman L. Allinger,*,† Lawrence R. Schmitz,‡ Ioan Motoc,§ Charles Bender,⊥ and Jan K. Labanowski⊥

Contribution from the School of Chemical Sciences, Department of Chemistry, University of Georgia, Athens, Georgia 30602, Department of Chemistry, Marshall University, Huntington, West Virginia 25755, Bristol-Myers Squibb Corporation, Pharmaceutical Research Institute, Core Chemistry Resources, Princeton, New Jersey 08543-4000, and Ohio Supercomputer Center, 1224 Kinnear Road, Columbus, Ohio 43212-1163. Received April 15, 1991

Abstract: Heats of formation may be calculated by many different schemes, and a scheme that may be used with the ab initio method is herein outlined in detail. The method is essentially the same as that which is used with MM2 and MM3, although the numerical quantities that go into the calculation are somewhat different. The method can be applied in either of two ways. Either a bond energy scheme in the usual sense is employed, with the vibrational energies being absorbed in the bond energy increments, or one may explicitly consider these quantities. The first method is applied to 6-31G* Hartree–Fock calculations on alcohols and ethers, and it fits the experimental data on 28 compounds to a root-mean-square error of 0.52 kcal/mol, while the fit to a group of anomeric compounds is poorer.

Introduction

The heats of formation of organic compounds are important physical properties. Because the number of experimental values being determined in recent years has become quite small, the practical importance of being able to use calculational methods to obtain these data has been increasing. A previous publication[1] has shown that by utilizing ab initio calculations at the 6-31G* level, and a bond energy scheme based on the concept of homodesmic equations, one can calculate heats of formation for saturated hydrocarbons and for a wide variety of aliphatic amines with probable errors of less than 1 kcal/mol. In the present work we have extended these calculations to cover simple oxygen compounds, alcohols, and ethers, so as to ascertain the presence or absence of any adverse effect on the calculations resulting from

the additional lone pairs of electrons in these molecules. Future papers will deal with compounds containing heavier atoms, conjugated systems, and special problems.

The difficulties in trying to calculate heats of formation by ab initio methods directly are well-known.[2] Much of the difficulty can be circumvented using the ideas described in the paragraph above (first suggested by Wiberg[3] and by Ibrahim and Schleyer[4]), and the necessary theory here has been developed in detail.[5] The

† University of Georgia.
‡ Marshall University.
§ Pharmaceutical Research Institute.
⊥ Ohio Supercomputer Center.

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