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Studies on Electron Spin Resonance Spectra of 2-Substituted Prop-2-yl Radicals

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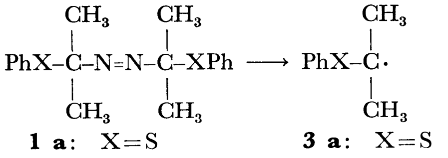
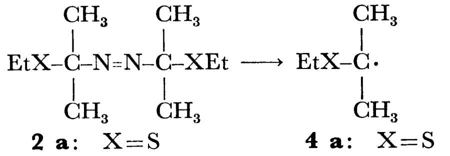
Electron spin resonance spectra of 2-substituted prop-2-yl radicals have been obtained. The substituents reported herein are phenylthio, phonoxy, benzyl, ethylthio, ethoxy, and *n*-propyl groups. Spectra were not obtained for phenylthio- and ethoxy-substituted radicals. It has been elucidated that α-heteroatoms greatly delocalize the odd electron. The mechanism of heteroatom-participation is discussed. Time dependency of intensities of signals in ESR spectra has revealed a qualitative order of the lifetime of these free radicals.

Kinetic studies on decompositions of 2-substituted azobis-2-propane (**1** and **2**) have revealed that the stability of a free radical increases in the order $CH_2 \lesssim O < S$, and the results have been discussed in view of the effect of heteroatoms on the radical center.[1] The argument was based on enthalpies of activation of decompositions. Thus, in order to elucidate the absolute order of stabilities of these free radicals, we must know the quantitative order of ground-state stabilities of azo compounds. This involves difficulties, since we need data on heats of formations of solutions.



$$\mathrm{PhX{-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}XPh} \longrightarrow \mathrm{PhX{-}C(CH_3)_2\cdot}$$

1 a: X=S **3 a**: X=S
b: X=O **b**: X=O
c: $X=CH_2$ **c**: $X=CH_2$



$$\mathrm{EtX{-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}XEt} \longrightarrow \mathrm{EtX{-}C(CH_3)_2\cdot}$$

2 a: X=S **4 a**: X=S
b: X=O **b**: X=O
c: $X=CH_2$ **c**: $X=CH_2$

Another problem exists in the assumption that activation parameters of decompositions of azo compounds exemplify the effect of stabilities of free radicals being produced.[2]

It is well known that hyperfine splitting constants (a_H^i) in ESR spectra of free radicals are well correlated to spin densities of the unpaired π-electrons (ρ_c^i) on carbon atoms by means of McConnell's equation[3]

$$a_H^i = Q\rho_c^i \qquad (1)$$

where Q is almost constant for similar radicals. Since the degree of delocalizations of π-electrons is a very important measure of stabilities of free radicals, a_H^i would present valuable information.

This paper deals with a discussion on the effect of heteroatoms on a carbon-radical center from the viewpoint of ESR spectroscopy. Qualitative discussion is given on lifetimes (or more precisely, reactivities) of free radicals under a certain condition.

Results

A 0.25 M solution of an azo compound in benzene was irradiated with light from a 100 W high-pressure mercury lamp (principal wavelength 3150 and 3660 Å) at room temperature in a cavity of ESR spectrometer. This technique is essentially suitable for generating free radicals. It produces free radicals in high concentration which makes it possible to detect them at elevated temperatures and free radicals of unequivocal and desired structure can be generated, which is an advantage over the technique of hydrogen abstraction. As an example, free radical **3c** cannot be generated predominantly by hydrogen abstraction reaction, because a benzylic hydrogen is more reactive than (or at least comparable to) the tertiary hydrogen.

The ESR spectrum of 2-phenoxyprop-2-yl (**3b**) was obtained with a good signal-to-noise ratio (Fig. 1) and showed a septet of intensity ratios 1 : 6 : 15 : 20 : 15 : 6 : 1. Other spectra so far obtained had signals attributable to structures **3** and **4**. However, none of them showed splittings due to aromatic protons or ethyl protons.[4]

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[2] W. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y. (1966), p. 128.

[3] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[4] Similar results have been reported: J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

No signal from **3a** was obtained when a solution of **1a** was subjected to measurement. Neither a change of solvent nor the lowering of temperature (≥ −100°C) could achieve the detection of signals. This suggests that the fade of **3a** is much faster than that of **3b** under the condition. Similarly, we could not obtain signals from a solution of **2b** at room temperature, but ethyl radical was detected at −196°C.[5,6] The results are summarized in Table 1.

It has been demonstrated that a free radical **3b** is fairly long-lived. As seen in Fig. 2, the most intense signal from this radical remains detectable after the irradiation with light has stopped. Signals from **3c** and **4c** are detectable only during irradiation. In contrast, the intensities of signals from **4a** decreases in prolonged irradiation, indicating rapid fade of this radical (Fig. 3).

Table 1. Hyperfine splitting constants and *g*-values of 2-substituted prop-2-yl radicals

Radical	a, G		*g*-Value	No. of Signals	
	CH_3	CH_2		Found	Theoret.
3a	—	—	—	—	—
3b	20.20		2.00324	7	7
3c	23.12	18.26	2.00263	17	21
4a	19.50		2.00359	7	7
4b	—	—	—	—	—
4c	22.2	17.8	2.0025	17	21

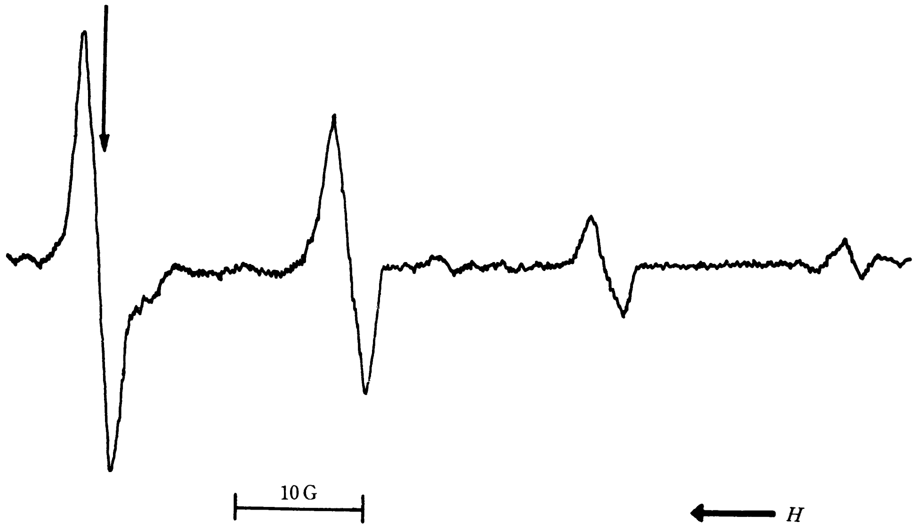

Fig. 1. ESR spectrum of 2-phenoxyprop-2-yl radical at room temperature. The arrow points to the center of the spectrum.

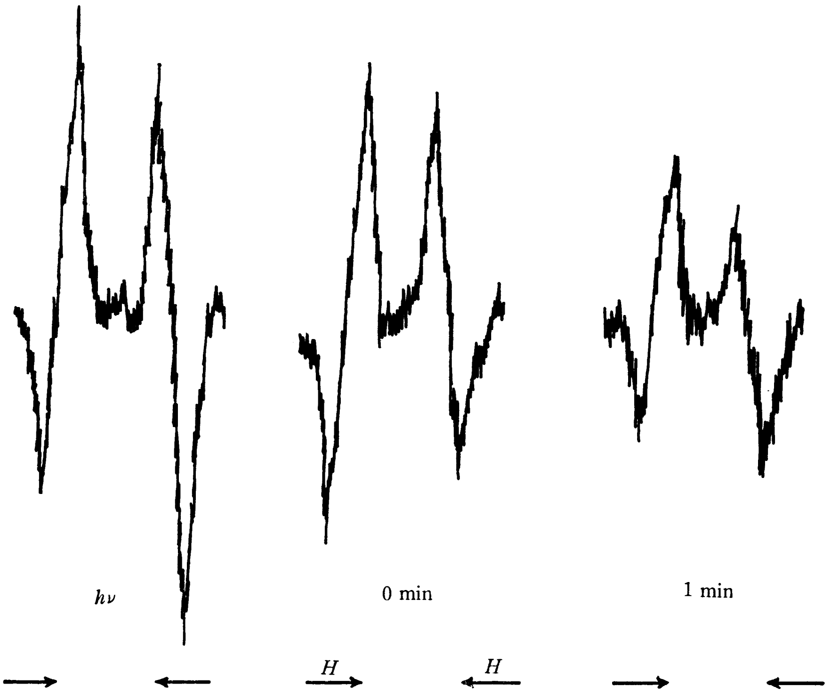

Fig. 2. Time-dependency of intensity of the most intense signal from **3b**.

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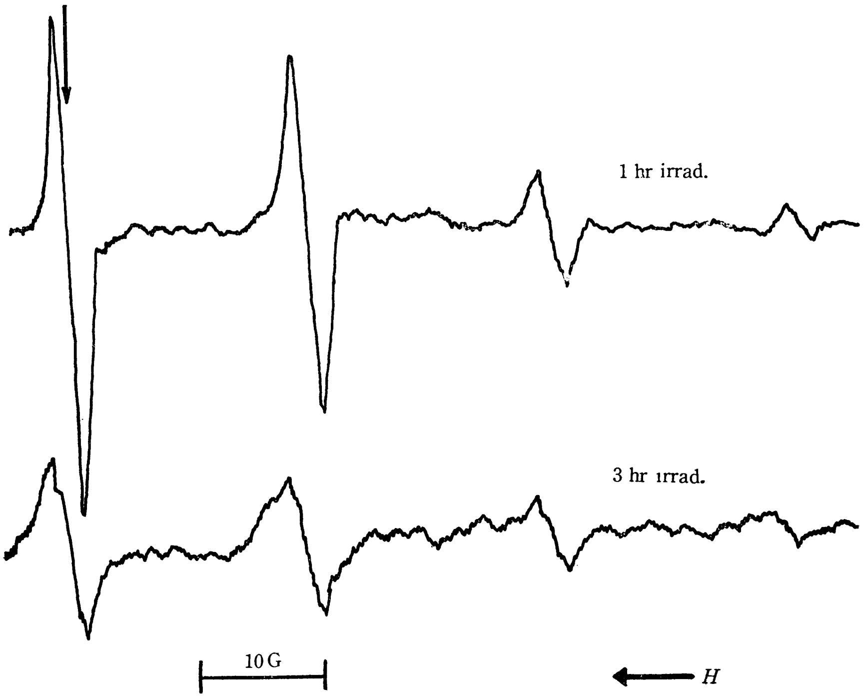

Fig. 3. ESR spectrum of 2-ethylthioprop-2-yl radical at room temperature. The arrow points to the center of the spectrum.

Discussion

As seen in Table 1, there exists a good agreement between hyperfine splitting constants and *g*-values for **3c**, **4c**, and *t*-butyl radical (22.7 gauss)[7] as well as for **3b** and 2-hydroxyprop-2-yl radical (20.0 gauss).[8] This enables us to compare the effect of heteroatoms on radical centers by using hyperfine splitting constants due to β-hydrogens in the absence of data on **3a** and **4b**. However, this situation does not hold, at least with an α-hydrogens (Table 2).

TABLE 2. HYPERFINE SPLITTING CONSTANTS OF SUBSTITUTED METHYL RADICALS

Radical	a_α, G	Ref.
$PhS\dot{C}H_2$	16.5	10
$PhO\dot{C}H_2$	17.7	10
$PhCH_2\dot{C}H_2$	22.0	4
$HS\dot{C}H_2$	19	9
$HO\dot{C}H_2$	17.2	8
$HCH_2\dot{C}H_2$	22.4	7

It has been also established that, as far as hyperfine splitting constants due to β-hydrogen are concerned, the value of Q in Eq. (1) is not affected by α-substituents.[11] Thus, we can use hyperfine splitting constants directly as a measure of spin delocalization, which increases in the order $S \gtrsim O > CH_2$ with the present series of free radicals. The corresponding *g*-values also support this order.[11,12]

The fact that, despite the large difference in spin-orbit coupling constants ($\zeta_S = -382\ cm^{-1}$, $\zeta_O = -152\ cm^{-1}$),[13] *g*-values of **3b** and **4a** do not differ a great deal suggests larger σ-character for the orbital containing an odd electron in **4a** than that in **3b**.[14] An alternative interpretation is, of course, possible: Smaller delocalization of an odd electron in **4a** than that in **3b**. However, the latter cannot explain results of kinetics[1] and others.[15]

It is interesting to compare the order of stabilities of radicals from the viewpoint of spin delocalization ($S > O \gtrsim CH_2$) with that obtained from activation parameters of decomposition of parent azo compounds ($S \gtrsim O > CH_2$). Although qualitative orders are the same for both cases, semi-quantitative orders are somewhat different with respect to positions of the oxygen-containing radical. We believe that this is attributable to larger electronegativity of oxygen than that of sulfur and methylene group. If the resonance effects of oxygen and sulfur were the same, the spin density on the carbon atom is expected to be smaller in the oxygen-containing radical than in its sulfur analog, because a larger inductive effect of oxygen than sulfur reduces more spin density on the former through a

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σ-bond.[14] This in turn, predicts larger resonance effect for sulfur than for oxygen from the fact that these radicals have nearly equal hyperfine splitting constants. Since free radicals generated here are essentially neutral, the inductive effect of a heteroatom does not change significantly, from the starting azo compounds to the transition states of the decompositions. Thus, activation parameters hardly reflect inductive effects of heteroatoms. It has been reported that the substituent effect in decompositions of substituted azobiscumenes is correlated to the Hammett relationship with σ_R.[16] Consequently, kinetic order represents stabilization by resonance participation, while spectral order that by net electronic effect. The larger σ-character of the sulfur-containing radical than its oxygen analog does not contradict this conclusion, since potential *d-sp*^{3} overlapping is suggested for sulfur-carbon π-bonding.[17–19]

In addition, the time-dependency of signal intensities predicts qualitative order of life-times of free radical as

$$\mathbf{3b} > \mathbf{3c} \approx \mathbf{4c} > \mathbf{4a} (> \mathbf{3a})$$

Thus, we have found that reactivities of these radicals under photolytic conditions are quite different from their thermodynamic stabilities.

Experimental

Materials. Compounds **1a**, **1b**, **1c**, and **2a** were prepared as described previously.[15,20,21]

Azobis(2-ethoxy)-2-propane (**2b**): Into a 300 m*l* round-bottomed flask equipped with a condenser and a stirrer were placed 150 m*l* of anhydrous ethanol and 5.1 g (0.22 g-atom) of sodium metal. Azobis(2-chloro)-2-propane (18.2 g, 0.1 mol) was added slowly to sodium ethoxide at the temperature of ice-water. Exothermic reaction occurred gradually in 2 hr, and the reaction mixture then turned to milky white. The mixture was stirred for additional 2 hr to complete the reaction. Excess ethanol was evaporated under reduced pressure. After filtration, the filtrate was poured into ice-water, and organic material was then extracted with ether. Careful distillation under reduced pressure yielded 2.5 g (11% yield) of pure **2b**, bp 70.5—71.0°C/12 mmHg.

Found: C, 59.06; H, 10.73; N, 15.72%. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 15.82%.

Azobis(2-propyl)-2-propane (**2c**): 2-Methylpentylamine (bp 100—104°C) was prepared from the corresponding alcohol according to Ritter and Kalish.[22] Sulfuryl chloride (13 g) in 10 m*l* of dry *n*-hexane was added dropwise to the amine (21 g) in *n*-hexane at the temperature of ice-water. After the addition had been completed, the organic layer was washed with water several times and dried over Drierite. Resulting crude sulfone amine (7.0 g) was used for the foregoing reaction without further purification. A mixture of the sulfone amine (7.0 g) in 50 m*l* of *n*-hexane and 150 m*l* of sodium hypochlorite (10% efficiency) was continuously stirred for 35 hr at room temperature. The organic layer was washed with water and dried over Drierite. Distillation under reduced pressure yielded 2 g (38% yield) of **2c**, bp 76—80°C/15 mmHg.

Found: C, 72.45; H, 13.40%. Calcd for $C_{12}H_{26}N_2$: C, 72.66; H, 13.21%.

Spectrometry. A 0.25 M solution of an azo compound in benzene was placed in 5 mm-o.d. quartz tube, which was thoroughly degassed by the thawing and freezing method. The sample tube was then sealed. The light from a 100 W high-pressure mercury lamp was focused on the sample in the cavity of the ESR spectrometer.

ESR spectra of generated radicals were measured at room temperature with a X-band, JES-3BX type spectrometer (Japan Electron Optics Laboratory Co., Ltd.) with 100 KHz field modulation. Magnetic-field-calibration markers were placed directly on the recorded spectrum by noting the occurrence of the proton resonance at a particular oscillator frequency which was then measured with a Hewlett-Packard frequency counter, Model 5245L.

2-Phenylthioprop-2-yl (**3a**): No signal was detected when a solution of **1a** in benzene, toluene, tetrahydrofuran or acetonitrile was subjected to measurement at various temperatures ($\geqslant -100$°C). An unidentified broad signal was observed at -196°C only when 2-methyltetrahydrofuran was used as a solvent. The signal is due to neither a benzenethiyl radical, nor a radical from the solvent, since the obtained *g*-value was 2.0026.

2-Phenoxyprop-2-yl (**3b**): After a few minutes irradiation with light, signals appeared on the first run of the spectrum. Signal intensities increased with prolonged irradiation period and a well-resolved spectrum was obtained within 2 hr. The spectrum showed a septet of relative intensity ratios 1.4 : 5.9 : 15.5 : 20.0 : 15.7 : 5.8 : 1.2, which were in good agreement with thoeretical values. The most intense signal from the radical remained detectable even after irradiation with light had been stopped. This kind of observation was obtained exclusively when 2-phenoxyprop-2-yl was applied in these studies.

2-Benzylprop-2-yl (**3c**): A spectrum resulting from the irradiation for 2 hr consisted of 17 lines of relative intensity ratios from the center of the spectrum to the wing; 20 : 9.3 : 9.7 : 14.3 : 3.6 : 7.5 : 5.7 :— : 3.6 : 1.8 : —. No resolvable hyperfine interaction was observed with the aromatic hydrogens in **3b** and **3c** with a modulation of 1 gauss.

2-Ethylthioprop-2-yl (**4a**): A spectrum obtained by irradiation for 2 hr exhibited a septet of relative intensity ratios close to the theoretical ones. Signal intensities decreased with a prolonged irradiation period. Splittings due to ethyl protons were not detected in the radical with a modulation of 0.5—1.0 gauss.

2-Ethoxyprop-2-yl (**4b**): When a solution of **2b** in *n*-pentane or isopentane was subjected to measurement, no signal was investigated at temperatures above -80°C. A well-resolved spectrum consisting of 12 lines (triplets of quartets) was obtained at -196°C, which was attributable to ethyl radical rather than **4b**. Observed hyperfine coupling constants ($a_\alpha = 22.4$ and $a_\beta = 26.7$) and *g*-value (2.0026) were in good agreement with those of previous studies.[4,7]

2-Methylpent-2-yl (**4c**): A similar type of spectrum with **3c** was obtained when **2c** was irradiated with light in benzene. No resolvable hyperfine interaction with 7-hydrogens was observed with a modulation of 0.5 gauss.

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19) Only 2*p*–2*p* π-overlapping or a canonical form of $-\overset{+\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}-\overline{\mathrm{C}}\langle$ is possible for the oxygen analog.

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