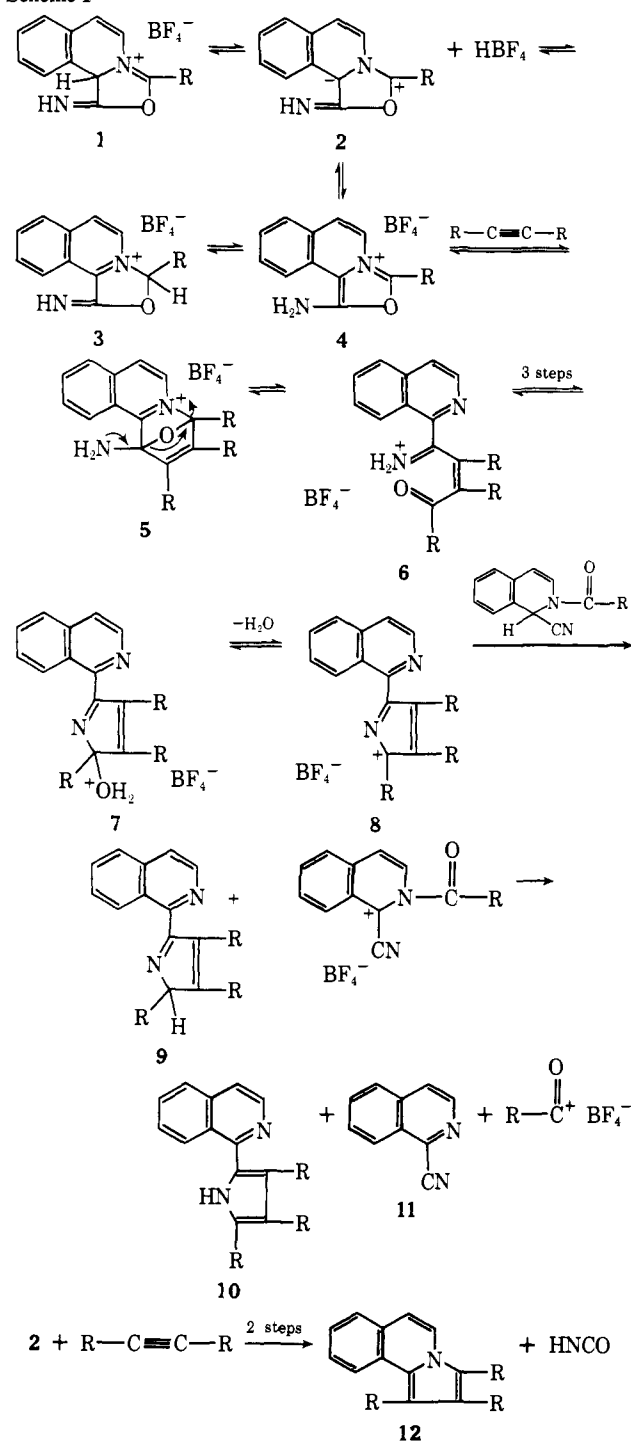


Scheme I



figurations of the respective energy profiles hold true when an alkene is used as the substrate. Thus, under conditions whereby the reactions are forced to completion, alkynes mainly form products of type **12**, and alkenes form products of type **10**.

An independent and unambiguous synthesis of **12** ( $\text{R} = \text{C}_6\text{H}_5$ ) has been achieved. The lithium salt of 1-benzylisoquinoline was caused to react with 2-( $\alpha$ -bromobenzyl)-2-phenyl-1,3-dioxolane (the ethylene glycol ketal of desyl bromide), and the mixture of reaction products was treated with polyphosphoric acid. A small quantity (*ca.* 2%) of **10** ( $\text{R} = \text{C}_6\text{H}_5$ ) was isolated from the reaction mixture. Its ir and nmr spectra were identical with those of the product obtained by the

reaction of **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) with tolan, and a mixture melting point test of the two samples showed no depression.

*p*-Nitrostilbene has been caused to react with **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) in DMF solution for 18 hr at  $100^\circ$ , and 2-(1-isoquinolyl)-3-*p*-nitrophenyl-4,5-diphenylpyrrole was isolated in 45% yield. The structure of the product was proved by its conversion *via* the amino derivative and its diazonium salt to be the known<sup>11</sup> 2-(1-isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole. The reaction of *p*-methoxystilbene with **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) under the same conditions as specified for the corresponding reaction of *p*-nitrostilbene gave 2-(isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole in 18% yield and 2-(1-isoquinolyl)-4-*p*-anisyl-3,5-diphenylpyrrole in 9% yield. The reaction of **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) with *p*-methoxytolan in refluxing DMF solution for 24 hr gave, in 12% yield, a mixture of 1,3-diphenyl-2-*p*-anisylpyrrolo[2,1-*a*]isoquinoline and 2,3-diphenyl-1-*p*-anisylpyrrolo[2,1-*a*]isoquinoline in a ratio of 1:2. There was also obtained, in 5.4% yield, a mixture of 2-(1-isoquinolyl)-3,5-diphenyl-4-*p*-anisylpyrrole and 2-(isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole in a ratio of about 35:65. Under the same reaction conditions, **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) and *p*-nitrotolan gave, in 31% yield, a mixture of 2,3-diphenyl-1-*p*-nitrophenylpyrrolo[2,1-*a*]isoquinoline and 1,3-diphenyl-2-*p*-nitrophenylpyrrolo[2,1-*a*]isoquinoline in a ratio of about 2:1. Also, there was obtained, in 7.3% yield, a mixture of 2-(1-isoquinolyl)-4-*p*-nitrophenyl-3,5-diphenylpyrrole and 2-(1-isoquinolyl)-3-*p*-nitrophenyl-4,5-diphenylpyrrole in approximately a 1:1 ratio. The formation of mixtures of isomers in most of these reactions indicates that the initial condensation reactions involve essentially synchronous formation of two new covalent bonds in each ring closure, as indicated in previous publications.<sup>4-6</sup> The structures of all of the products cited above were proved by unambiguous methods.

**Acknowledgment.** This work was supported in part by grants from the National Institutes of Health and the National Science Foundation.

William E. McEwen,\* Paul E. Stott, Charles M. Zepp  
Department of Chemistry, University of Massachusetts  
Amherst, Massachusetts 01002  
Received July 19, 1973

### Correlation between Deuterium and Carbon-13 Relaxation Times. A Convenient Means to Determine the Mechanism of <sup>13</sup>C Relaxation and <sup>2</sup>H Quadrupole Coupling Constants

Sir:

The dominant contribution to <sup>13</sup>C magnetic relaxation comes from the <sup>13</sup>C-<sup>1</sup>H dipole-dipole interaction, except for very small molecules or rapidly rotating methyl groups where spin-rotation interaction has also to be considered. Scalar interaction and chemical shift anisotropy usually do not contribute significantly to the <sup>13</sup>C relaxation of protonated carbons.<sup>1,2</sup> If

(1) (a) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(2) (a) G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972); (b) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *ibid.*, **95**, 1527 (1973).

**Table 1.** Comparison of Measured  $^{13}\text{C}$  Spin-Lattice Relaxation Times with Those Calculated from  $^2\text{H}$  Relaxation Times, and Evaluation of Quadrupole Coupling Constants

		Spin-lattice relaxation times ( $T_1$ ) (sec)					Quadrupole coupling constant ( $e^2qQ/\hbar$ , kHz)		
		$^{13}\text{C}$		Temp, °C	Ref				
$^2\text{H}$		Calcd <sup>a,b</sup>	Obsd			Calcd <sup>c</sup>	Obsd	Ref	
<i>N,N</i> -Dimethylformamide	$\text{CH}_3$ (cis)	3.04	20.2	17.8 <sup>c</sup>	25	2a	160		
	$\text{CH}_2$ (trans)	1.62	10.7	10.5 <sup>c</sup>	25	2a	168		
	CHO	0.95	18.9	19.5 <sup>c</sup>	25	2a	173		
Acetic acid	$\text{CH}_3$	1.46 <sup>f</sup>	9.7	9.8 <sup>c</sup>	35	10b	176	168 ± 10	<i>g</i>
Cyclohexane	$\text{CH}_2$	1.47 <sup>f</sup>	14.6	17.0 <sup>c</sup>	36	2b	183	174 ± 2	<i>h</i>
Phenylacetylene	$\equiv\text{CH}$	0.25	7.8	9.3 <sup>c</sup>	38	2b	254	215 ± 5	<i>i</i>
Benzene	CH	1.52	33.9	29.3 <sup>c</sup>	38	2b	172	186 ± 1.6	<i>j</i>
Toluene	$\text{CH}_3$	5.04	33.4	16.3 <sup>d</sup>	38	2b			
Nitrobenzene	$\text{C}_\alpha\text{-H}$	0.58	13.0	6.9 <sup>d</sup>	38	2b			
	$\text{C}_\gamma\text{-H}$	0.39	8.7	4.8 <sup>d</sup>	38	2b			

<sup>a</sup> Corresponding to temperature 30°. <sup>b</sup> Quadrupole coupling constants used: 170 kHz for  $\text{sp}^3$ , 180 kHz for  $\text{sp}^2$ , and 215 kHz for  $\text{sp}$ . <sup>c</sup> Degassed samples. <sup>d</sup> Undegassed samples. <sup>e</sup> Estimated error 10%. <sup>f</sup> Glasel's data, ref 9. <sup>g</sup> M. de Graca, C. Dillon and J. A. S. Smith, *J. Chem. Soc., Faraday Trans. 2*, 2183 (1972). <sup>h</sup> J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3422 (1965). <sup>i</sup> P. Pykko, *Ann. Univ. Turku, Ser. A*, **88**, 93 (1966). <sup>j</sup> P. L. Olympia, Jr., I. V. Wei, and B. M. Fung, *J. Chem. Phys.*, **51**, 1610 (1966).

more than one mechanism contributes to the relaxation of a given  $^{13}\text{C}$  nucleus, the dipole-dipole contribution can be estimated by measurement of the nuclear Overhauser enhancement.<sup>3</sup> In contrast to  $^{13}\text{C}$  and  $^1\text{H}$  the only significant contribution to the relaxation of  $^2\text{H}$  (D) arises from the motional modulation of the interaction between the quadrupole moment and the electric field gradient at the nucleus.<sup>4</sup> Since both  $^2\text{H}$  and  $^{13}\text{C}$  relaxation comes from intramolecular interactions, a comparison of the corresponding  $^2\text{H}$  and  $^{13}\text{C}$  relaxation times should provide an alternative means of estimating the contribution to  $^{13}\text{C}$  relaxation arising from interactions other than dipole-dipole. Furthermore, for those cases where the  $^{13}\text{C}$  relaxation time has been shown to be dominated by the dipole-dipole interaction, a comparison of the corresponding  $^2\text{H}$  and  $^{13}\text{C}$  relaxation times provides a new method for calculating the quadrupole coupling constant.<sup>5,6</sup> The  $^2\text{H}$  spin-lattice relaxation times were measured on a Varian XL-100 spectrometer by the inversion-recovery method<sup>7</sup> using a  $180^\circ\text{-}\tau\text{-}90^\circ$  pulse sequence. The deuterium relaxation time  $T_1(^2\text{H})$  is related to the effective correlation time  $\tau_c$  of the molecular reorientation as follows<sup>4</sup>

$$1/T_1(^2\text{H}) = 3(e^2qQ/\hbar)^2\tau_c/8 \quad (1)$$

where  $e^2qQ/\hbar$  is the deuterium quadrupole coupling constant. The  $^{13}\text{C}$  spin-lattice relaxation time  $T_1(^{13}\text{C})$  due to the dipole-dipole relaxation is given by<sup>8</sup>

$$1/T_1(^{13}\text{C}) = N\hbar^2\gamma_C^2\gamma_H^2r^{-6}\tau_c \quad (2)$$

where  $N$  is the number of hydrogens attached to the corresponding carbon,  $\gamma_C$  and  $\gamma_H$  are the magnetogyric ratios for  $^{13}\text{C}$  and  $^1\text{H}$ , respectively, and  $r$  is the distance

(3) K. F. Kuhlman, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

(4) A. Abragam, "The Principles of Nuclear Magnetism," Oxford, 1961, Chapter 8.

(5) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York, 1969.

(6) For a recent compilation of data, see (a) H. Saitô, I. C. P. Smith, and H. H. Mantsch, *Progr. Nucl. Magn. Resonance Spectrosc.*, in preparation; (b) F. S. Millett and B. P. Dailey, *J. Chem. Phys.*, **56**, 3249 (1972).

(7) (a) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968); (b) R. Freeman and H. D. W. Hill, *ibid.*, **54**, 3367 (1971).

(8) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

between the hydrogen and carbon atoms. Both eq 1 and 2 apply for the condition of extreme narrowing. By combining eq 1 and 2 we obtain

$$\frac{T_1(^{13}\text{C})}{T_1(^2\text{H})} = \frac{3}{8} \frac{r^6(e^2qQ/\hbar)^2}{N\hbar^2\gamma_C^2\gamma_H^2} \quad (3)$$

Equation 3 can be rewritten as

$$T_1(^{13}\text{C})/T_1(^2\text{H}) = 19.9/N \quad (4)$$

assuming a C-H bond distance of 1.09 Å and a quadrupole coupling constant of 170 kHz<sup>5,6</sup> for the  $\text{sp}^3$  C-D bond. A comparison of  $^{13}\text{C}$  relaxation times calculated using eq 3 and the corresponding deuterium relaxation data<sup>9</sup> with the experimental values<sup>2,10</sup> is given in Table I. The agreement between observed and predicted values of  $T_1$  is excellent for degassed samples.<sup>11</sup> Some discrepancies appear in the case of undegassed samples used for  $T_1(^{13}\text{C})$  measurements. Thus, we may conclude that in many cases the values of  $T_1$  for  $^{13}\text{C}$  can be predicted from those of  $^2\text{H}$  and *vice versa*. A recent chemical application of this technique has been described.<sup>12</sup>

On the other hand, if both the  $^2\text{H}$  and  $^{13}\text{C}$  relaxation times are known, the quadrupole coupling constant  $e^2qQ/\hbar$  may be calculated from eq 3. Previous attempts<sup>13</sup> to determine quadrupole coupling constants from combined  $^1\text{H}$  and  $^2\text{H}$  relaxation data gave poor results because of difficulty in separating various intramolecular contributions. Furthermore, it was gen-

(9) The removal of dissolved oxygen in samples was unnecessary as shown in the following examples. The  $T_1(^2\text{H})$  values of degassed samples are taken from Glasel (J. A. Glasel, *J. Amer. Chem. Soc.*, **91**, 4569 (1969)):  $T_1$  (toluene- $d_6$ ) 5.04 sec (undegassed), 5.11 sec (degassed);  $T_1$  (acetone- $d_6$ ) 4.74 sec (undegassed), 4.78 (degassed);  $T_1$  (benzene- $d_6$ ) 1.52 (undegassed), 1.45 sec (degassed).

(10) (a) T. D. Alger, D. M. Grant, and J. R. Lyerla, Jr., *J. Phys. Chem.*, **75**, 2539 (1971); (b) T. D. Alger and D. M. Grant, *ibid.*, **75**, 2538 (1971).

(11) Both  $^{13}\text{C}$  and  $^2\text{H}$  relaxation times are temperature dependent as predicted by the Stokes-Einstein equation,<sup>4</sup>  $\tau_c = 4\pi\eta a^3/3kT$  where  $\eta$  is the viscosity of the liquid,  $a$  is the radius of a spherical molecule,  $T$  is the temperature, and  $k$  is the Boltzmann constant. Strictly speaking a comparison should be made only of measurements taken at the same temperature.

(12) H. H. Mantsch, H. Saito, and I. C. P. Smith, *J. Amer. Chem. Soc.*, in press.

(13) (a) D. Woessner, *J. Chem. Phys.*, **40**, 2341 (1964); (b) G. Bonera and A. Rigamonti, *ibid.*, **42**, 175 (1965); (c) M. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965); (d) R. Figgins and M. Rhode, *Mol. Phys.*, **17**, 669 (1970).

erally necessary to assume isotropic motion. Molecules in the liquid state tumble anisotropically,<sup>14</sup> in most cases, and the dependence of the <sup>2</sup>H relaxation times on this anisotropic motion is not the same as that of <sup>1</sup>H.<sup>15</sup> The angular dependence of the <sup>13</sup>C-<sup>1</sup>H dipole-dipole relaxation is exactly the same as that of the C-D quadrupole relaxation,<sup>14b</sup> which makes it possible to compare values of *T*<sub>1</sub> for <sup>13</sup>C and <sup>2</sup>H under any kind of anisotropic motion. Table I shows the observed quadrupole coupling constants and those calculated from the <sup>2</sup>H and <sup>13</sup>C relaxation times. The agreement is excellent, within 5-7%, with the exception of phenylacetylene where a substantial contribution to <sup>13</sup>C relaxation from chemical shift anisotropy is expected. Thus, for small organic compounds, a comparison of the <sup>2</sup>H and <sup>13</sup>C spin lattice relaxation times provides a facile determination of the deuterium quadrupole coupling constant and mechanism of carbon relaxation.

(14) (a) W. T. Huntress, Jr., *Advan. Magn. Resonance*, **4**, 1 (1970);  
(b) W. T. Huntress, Jr., *J. Chem. Phys.*, **48**, 3524 (1968).

(15) Assink and Jonas (R. A. Assink and J. Jonas, *J. Magn. Resonance*, **4**, 347 (1971)) employed a selectively deuterated compound of geometry conducive to determination of the dependence of <sup>2</sup>H and <sup>1</sup>H relaxation times on the orientation of the rotational axes. This method cannot be used generally, however, especially when the rotational axes are not known.

(16) Visiting Scientist, from the Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan 248.

(17) Visiting Professor, from the Institute of Chemistry, University of Cluj, Cluj, Romania.

(18) Issued as NRCC Publication 13681.

Hazime Saitô,<sup>16</sup> Henry H. Mantsch,<sup>17</sup> Ian C. P. Smith\*

*Division of Biological Sciences  
National Research Council of Canada<sup>18</sup>  
Ottawa, Ontario, Canada K1A 0R6*

*Received August 21, 1973*

## Electron Paramagnetic Resonance Study of Free Radicals in an Adamantane Matrix. VII. Aromatic Hydrogen Addition Radicals

Sir:

In past studies of neutral free radicals in an adamantane matrix, the radicals have been formed by removal of an atom or group of atoms from the precursor molecule,<sup>1-17</sup> although we had noted previously that X-

- (1) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970).
- (2) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).
- (3) D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, **92**, 4115 (1970).
- (4) D. R. Gee and J. K. S. Wan, *Can. J. Chem.*, **49**, 20 (1971).
- (5) J. R. Ferrell, G. R. Holdren, Jr., R. V. Lloyd, and D. E. Wood, *Chem. Phys. Lett.*, **9**, 343 (1971).
- (6) R. V. Lloyd and D. E. Wood, *Mol. Phys.*, **20**, 735 (1971).
- (7) D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, **75**, 3486 (1971).
- (8) T. Richerzhagen and D. H. Volman, *J. Amer. Chem. Soc.*, **93**, 2062 (1971).
- (9) D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Amer. Chem. Soc.*, **93**, 4145 (1971).
- (10) S. W. Kanick, R. E. Linder, and A. C. Ling, *J. Chem. Soc. A*, 2971 (1971).
- (11) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).
- (12) D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, **94**, 9258 (1972).
- (13) D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).
- (14) This paper reports the hydrogen addition radical of cyclopentadiene: R. E. Linder and A. C. Ling, *Can. J. Chem.*, **50**, 3982 (1972).
- (15) R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, **95**, 2459 (1973).

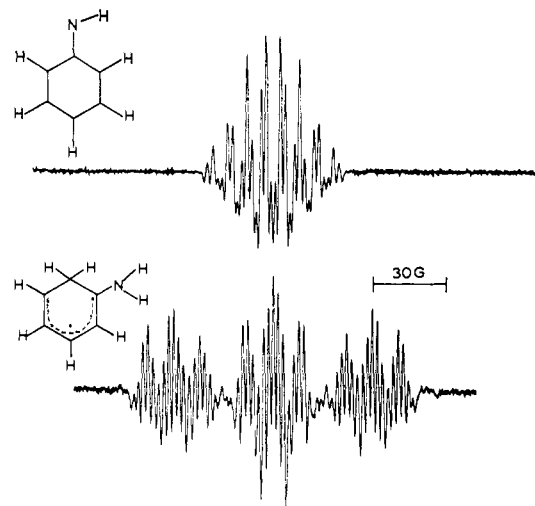


Figure 1. Second derivative epr spectra of anilino radical (top) and 1-aminocyclohexadienyl radical (bottom) in adamantane at room temperature. Both samples were from the same batch, but the upper one was treated for maximum R· radical and the lower one for maximum RH<sub>2</sub>· radical as described in the text.

irradiation of isobutylene in adamantane produced some *tert*-butyl radical,<sup>5</sup> thus at least suggesting that hydrogen atom addition to a precursor molecule could occur. We have now prepared hydrogen addition radicals from several aromatic molecules and have shown thereby that this is a general method of radical formation in adamantane. We have found that the details of sample preparation are critically important in determining the nature of the predominant radical produced, that is, a hydrogen abstraction radical (R·) or a hydrogen addition radical (RH<sub>2</sub>·). The factors in the sample preparation which favor R· suggested to us that hydrogen atom scavenging by atmospheric oxygen is occurring. To confirm this hypothesis we prepared degassed samples of adamantane containing molecules such as toluene, which can either lose a hydrogen to form benzyl radical or add a hydrogen to form methylcyclohexadienyl radicals. The X-irradiation of degassed samples produced a large predominance of RH<sub>2</sub>· whereas the samples prepared without the exclusion of air produced a predominance of R·. Inclusion of I<sub>2</sub>, which can act as a hydrogen atom trap, in degassed preparations then dramatically decreased the yield of RH<sub>2</sub>· but did not noticeably affect the yield of R·. Use of adamantane-*d*<sub>16</sub> 96% D as a matrix for preparation of RH<sub>2</sub>· resulted in about equal amounts of deuterium and hydrogen atom incorporation, thus demonstrating that some of the hydrogen atoms are produced in the bulk adamantane by the radiolysis and suggesting that a very large negative deuterium isotope effect may be involved.

The technique for preparation of R· in cases where RH<sub>2</sub>· can also be formed involves rapid crystallization of the adamantane by cooling a solution of the desired precursor saturated with prepurified adamantane<sup>6</sup> and with air (or even better with oxygen). The recrystallized adamantane is then vacuum filtered almost to dryness and X-irradiated directly in air. This usually results in >20/1 ratio of R·/RH<sub>2</sub>·. For hygroscopic

(16) D. M. Camaioni, H. F. Walter, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 4057 (1973).

(17) D. E. Wood and R. F. Sprecher, *Mol. Phys.*, in press.