Rates of Termination of Radicals in Solution. VII.[1] Allylic Radicals

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Abstract: The rate constants for bimolecular decay of allyl, 2-methallyl, and *cis*- and *trans*-1-methallyl radicals in liquid propene, isobutene, and *cis*- and *trans*-2-butene, respectively, have been determined over a wide temperature range from near the boiling points of the solvents to about −120° using the esr–rotating sector technique. The values, which range from 10^9 to 10^{10} M^{-1} sec^{-1}, were compared with the encounter rate constants calculated from density and viscosity data. We conclude that the self-termination of allyl, 2-methallyl, and *trans*-1-methallyl radicals fits the diffusion-controlled model. However, the rate constant for the *cis*-1-methallyl radical is unexpectedly high at the higher temperatures. The viscosities of liquid propene, isobutene, and *cis*- and *trans*-2-butene between their boiling points and −100° are reported.

We have extended our studies on the rates of termination of radicals in solution to allyl and methallyl radicals. Sufficiently high concentrations of these radicals for esr detection can be produced by photolysis of di-*tert*-butyl peroxide in the corresponding alkenes, and highly resolved esr spectra have been reported.[2,3] With propene, *cis*- and *trans*-2-butene, and isobutene only allylic radicals, resulting from hydrogen abstraction from the parent compounds by primarily formed *tert*-butoxy radicals, are observed. However, some addition of the *tert*-butoxy radical to the double bond of the olefin may also occur as a side reaction at higher temperatures.[4] Since allylic radicals are chemically more stable than the corresponding alkyl radicals, their bimolecular termination might conceivably be hindered by small activation barriers. In principle, an activation barrier can be determined by comparison of the measured termination rate constant, k, with the encounter rate constant, k_D, which in turn can be calculated using diffusion kinetic theory supplemented by semiempirical estimation of diffusion constants and collision diameters.[5] While the uncertainties in the determination of k_D do not allow determination of small activation barriers in the bimolecular termination of radicals with acceptable accuracy by comparison with the measured rate constant k at *one* temperature, such "extra" activation energies should be revealed by a different temperature dependence of k and k_D. We have, therefore, measured the rates of disappearance of allyl and methallyl radicals in the parent alkenes over temperature ranges of about 100° using the esr–rotating sector technique described previously,[1,6–8] and have compared the rate constants with calculated values of k_D.

Experimental Section

The esr experiments were carried out with static samples which were irradiated with uv light in the cavity of a Varian esr spectrometer. Allyl, *cis*-1-methallyl, *trans*-1-methallyl, and 2-methallyl radicals were produced by photolysis of di-*tert*-butyl peroxide (Matheson Coleman and Bell) in liquid propene, *cis*-2-butene, *trans*-2-butene, and isobutene, respectively. The samples were free of oxygen, and their temperatures were varied by means of the Varian variable-temperature accessory using gas stream cooling. The temperatures of the samples were 10–12° higher than those of the gas stream owing to heating by the intense irradiation. Since the radical decay rates were very fast, relatively high peroxide concentrations had to be used to obtain reasonable signal to noise ratios. Typical values were 0.27 M for propene and 0.55 M for the butenes. Experiments with lower and higher peroxide concentrations were also carried out at temperatures around −100 and −50°. Integrations of the esr spectra to determine the steady-state concentrations of the radicals were carried out at the lowest possible microwave powers compatible with a sufficiently high signal to noise ratio to avoid partial saturation of the spin systems. In the rotating sector experiments the decay of the radicals was recorded up to 70–80%.

At the high peroxide concentrations used in this work the previous assumption of a constant radical concentration over the cross-section of sample cell no longer holds. Instead there will be a concentration gradient from the front part of the sample cell to the back side. The esr absorption then is proportional to the mean value, $[\overline{R}]$, of the radical concentration over the cross-section of the sample cell. Even if the radicals decay exclusively by self-termination with a rate constant k after the light beam is cut off, so that locally the second-order law holds, where $[R]_0$ is the steady-state and $[\overline{R}](t)$ the

$$[R]_0/[R](t) = 1 + 2k[R]t \qquad (1)$$

time-dependent radical concentration, this simple law no longer holds for the decay of the esr signal. Instead, the ratio $[\overline{R}]_0/[\overline{R}](t)$ obtained from the esr signals increases somewhat faster with time than is predicted by introducing average concentration values in eq 1. The deviation depends on the optical density of the irradiated solution. However, we estimate that under our experimental conditions these deviations do not exceed 5% and, therefore, can be neglected since our experimentally determined decay rate constants have probable errors of ±20%.

The viscosities of the liquified gases with and without peroxide were determined with a modified Ostwald viscometer (Fenske–Canon, size 25) which was calibrated with pentane. A qualitative product analysis was carried out for the reaction in propene using glpc.

Results and Discussion

Our samples generally yielded good esr signal intensities for allyl, *trans*-1-methallyl, and 2-methallyl radicals over the temperature range employed. Figure 1 shows as an example the esr spectrum of the 2-meth-

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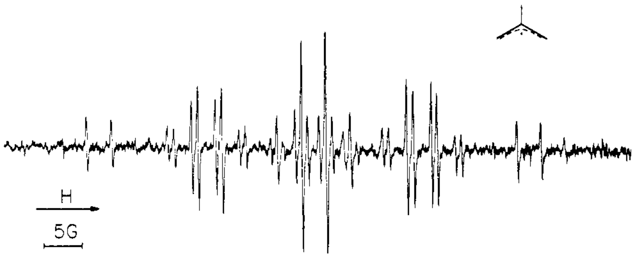

Figure 1. Esr spectrum of the 2-methallyl radical at −110° obtained by photolysis of 0.55 *M* di-*tert*-butyl peroxide in isobutene.

allyl radical at −110°. The decay of the esr signals, obtained by the rotating sector technique, followed the second-order law well. The spectra of the *cis*-1-methallyl radicals, however, became very weak at temperatures above −60°, and the decay data were inadequate to test the form of the rate law; consequently the data were force fitted to second-order kinetics. Since our splitting parameters determined at about −100° agree very well with values published previously,[2,3] they are not reported here.

The results given below are interpreted on the basis of the following reaction scheme (eq 2–8). Photolysis

$$(t\text{-BuO})_2 \xrightarrow{h\nu} \overline{2t\text{-BuO}\cdot} \qquad (2)$$

$$\overline{2t\text{-BuO}\cdot} \xrightarrow{k_r} \text{products} \qquad (3)$$

$$\overline{2t\text{-BuO}\cdot} \xrightarrow{k_d} 2t\text{-BuO}\cdot \qquad (4)$$

$$t\text{-BuO}\cdot + \text{RH} \xrightarrow{k_a} t\text{-BuOH} + \text{R}\cdot \qquad (5)$$

$$2t\text{-BuO}\cdot \xrightarrow{k_1} \text{products} \qquad (6)$$

$$t\text{-BuO}\cdot + \text{R}\cdot \xrightarrow{k_2} \text{products} \qquad (7)$$

$$\text{R}\cdot + \text{R}\cdot \xrightarrow{k_3} \text{products} \qquad (8)$$

of the peroxide yields two caged *tert*-butoxy radicals, which may recombine within the cage (eq 3) or diffuse apart (eq 4). The only observed allylic radicals are produced by the transfer reaction (eq 5), and radical termination occurs by the bimolecular reactions 6–8. We assume that reactions of the allylic radicals with the peroxide, with products already formed, and with radicals, which might be formed by reaction of *tert*-butoxy radicals with these products, can be neglected. This appears reasonable and is in accord with the results of Crawford and Al-Sader,[9] who found that allyl radicals produced by thermolysis of the corresponding azo compound at 150° in the gas phase yielded almost exclusively 1,5-hexadiene as a reaction product. The reaction of *tert*-butoxy radicals with allylic compounds is fast enough to prevent β-scission into methyl radicals and acetone and gives a nearly quantitative conversion to allyl radicals.[10] The rate constant, k_a, for the transfer reaction 5 has not been reported but its order of magnitude can be estimated. The rate constant for hydrogen abstraction from toluene was reported[10] as 8×10^4 and 8.3×10^3 M^{-1} sec^{-1} at 40° in CCl_4[11] with an activation energy of 5.6 kcal/mol.[11] Lower activation energies have also been reported (4.7[12] and 1.7 kcal/mol[13]). Since allylic hydrogens are six times more reactive toward *tert*-butoxy radicals than benzylic ones,[11] we expect $k_a \sim 10^5$ M^{-1} sec^{-1} at room temperature with an activation energy around 4 kcal/mol. Thus k_a is expected to be of the order of 10^4 M^{-1} sec^{-1} at −50° and 10^3 M^{-1} sec^{-1} at −100°. Reactions 2–8 then yield the kinetic equations

$$d[\text{R}']/dt = I\Phi - k_a[\text{R}'][\text{RH}] - k_2[\text{R}'][\text{R}] - 2k_1[\text{R}']^2 \qquad (9)$$

$$d[\text{R}]/dt = k_a[\text{R}'][\text{RH}] - k_2[\text{R}'][\text{R}] - 2k_3[\text{R}]^2 \qquad (10)$$

where R′ is the *tert*-butoxy radical. The quantity $I\Phi$ is the rate of photochemical production of *tert*-butoxy radicals. The quantum yield includes both inefficiency in the primary fission and that which arises from mutual destruction of geminate radical pairs within the solvent cage. Under our experimental conditions, where [RH] ∼10 *M* and the steady-state concentration $[\text{R}]_0$ of the allylic radicals was $2–5 \times 10^{-7}$ *M*, if we assume that k_1, k_2, and k_3 are all of the order of 10^9 M^{-1} sec^{-1}, we find $k_2[\text{R}]$ negligible compared with $k_a[\text{RH}]$. In order to check the validity of these assumptions, solutions of the peroxide in propene were irradiated under the conditions of the esr experiments and analyzed by glpc. The main products, identified by comparison of retention times with authentic samples, were *tert*-butyl alcohol and 1,5-hexadiene. A small amount of allyl *tert*-butyl ether was also detected. At short irradiation times (2 min) they accounted for 90% of all products found and appeared in the mol ratio 1:0.42:0.04, respectively. The minor remaining products are probably formed by secondary reactions. We have assumed that similar conditions hold for the systems involving methallyl radicals, so that the decay curves of their esr signals can also be analyzed using eq 1.

The decay rate constants, $2k_3$, for allyl radicals in propene solutions and for *trans*-1-, *cis*-1-, and 2-methallyl radicals in solutions in the corresponding butenes are presented in Figures 2 and 3 in an Arrhenius plot, and numerical values are tabulated in Table I. The rate constants are in the range 10^9–10^{10} M^{-1} sec^{-1} and follow the Arrhenius equation reasonably well. The activation energies, obtained by least-squares analysis,

Table I. Rate Constants for Decay of Allylic Radicals

Temp, °C	$2k[10^9\ M^{-1}\ \text{sec}^{-1}]$			
	Allyl	2-Methallyl	*trans*-1-Methallyl	*cis*-1-Methallyl
−8		7.8[a]	4.4	
−32		9.7	2.8	19[a]
−41	7.6		3.0	
−50		7.8	3.2	8.9[a]
−60		6.8		
−65	4.8			
−69		5.3	2.1	3.9
−93	4.3	2.7	1.2	2.7
−115	2.3	1.5	0.93	0.95
−130	1.5			

[a] Accuracy no better than ±50% because of low signal-to-noise ratio.

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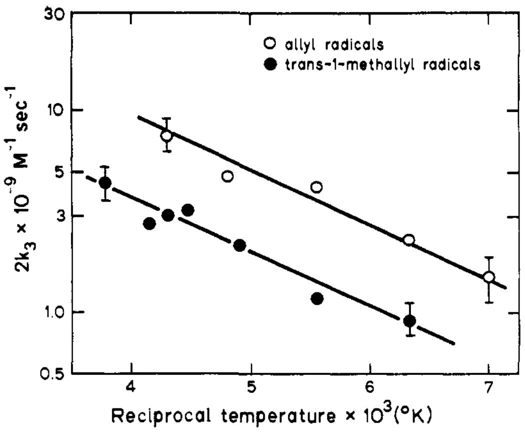

Figure 2. Arrhenius plots of decay rate constants for allyl and *trans*-1-methallyl radicals in their parent olefins with added peroxide.

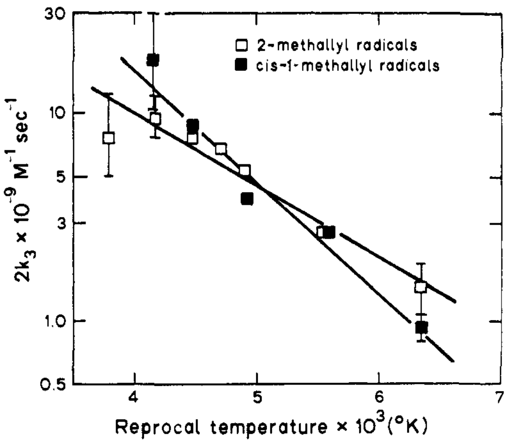

Figure 3. Arrhenius plots of decay rate constants for *cis*-1-methallyl and 2-methallyl radicals in their parent olefins with added peroxide.

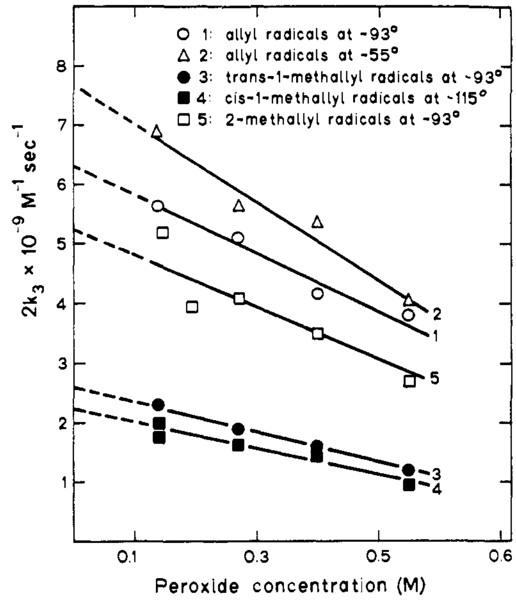

Figure 4. Dependence of the decay rate constants for allyl and *trans*-1-, *cis*-1-, and 2-methallyl radicals on di-*tert*-butyl peroxide concentration.

are 1.2 kcal/mol for allyl and *trans*-1-methallyl radicals, 1.6 kcal/mol for 2-methallyl radicals, and 2.4 kcal/mol for *cis*-1-methallyl radicals, with an experimental uncertainty of about ±20%. The decay rate constants depend on peroxide concentration as shown in Figure 4. At −100° all four radicals show an increase in $2k_3$ by a factor of about 2 when the peroxide concentration is lowered from the initial 0.55 *M* to 0 (linear extrapolation). The high s/n ratio obtained with allyl radicals allowed us also to study this effect at −55°, where the same increase was found. This effect, therefore, shows little or no temperature dependence.

Since the rates are of the order of magnitude expected from diffusion-controlled reactions, we have compared them with calculated encounter rates using the equation derived by Noyes[14]

$$k_D = \frac{4\pi N_0 \zeta D_{12}^0/1000}{1 + 4\pi N_0 \zeta D_{12}^0/1000k_c} \tag{11}$$

where N_0 is Avogadro's number; ζ is the encounter diameter; D_{12} is the mutual diffusion constant for a solute, 1, in a solvent, 2; and k_c is the rate constant that would be observed if diffusion were fast enough to instantaneously remove all concentration gradients established by reaction.

An upper limit to k_c is the calculated gas-phase encounter rate.[5] Several approaches to calculation of the quantity ζD_{12}^0 are suggested in the literature. We have assumed that the mutual diffusion coefficients for the radicals are approximately the same as the self-diffusion coefficients of the parent molecules. The latter are estimated using viscosity data and other calculable molecular parameters. Reid and Sherwood[15] have reviewed the subject and recommend use of Scheibel's semiempirical equation,[16] at least for solutions near room temperature. The Scheibel equation was used in our previous work.[5] Another formula has been suggested by Li and Chang[17]

$$D_{12}^0 = \frac{k_T}{\eta}\left(\frac{N_0}{V}\right)\frac{\sigma - \tau}{2\sigma} \tag{12}$$

where *V* is the molar volume, σ is the number of all closest neighbors, and τ is the number of closest neighbors in one layer of liquid. For cubic packing the quantity $(\sigma - \tau)/2\sigma$ is one-sixth.

We have applied both formulas to calculate self-diffusion coefficients of water and several alcohols, for which experimental values are available in the literature.[18,19] The Li and Chang formula gave better agreement with experimental data and was used to calculate diffusion coefficients and encounter rate constants for radicals in liquid alkenes assuming cubic packing. The densities which are required in the calculations are available[20] for propene over the entire temperature range. Densities of the butenes were reported by Gallant[21] over part of the temperature

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Table II. Kinematic Viscosity, ν, in Centistokes and Absolute Viscosity, η, in Centipoise for Propene, Isobutene, *cis*-2-Butene, and *trans*-2-Butene[a]

Temp, °C	Propene		Isobutene		*cis*-2-Butene		*trans*-2-Butene	
	ν	η	ν	η	ν	η	ν	η
−10			0.31	0.20	0.34	0.225	0.32	0.205
−20			0.34	0.22	0.37	0.25	0.34	0.225
−30			0.37	0.24	0.40	0.27	0.37	0.25
−40			0.41	0.27	0.44	0.30	0.40	0.275
−50	0.31	0.19	0.45	0.30	0.48	0.34	0.44	0.30
−60	0.34	0.21	0.50	0.34	0.54	0.38	0.49	0.35
−70	0.375	0.24	0.57	0.39	0.60	0.43	0.56	0.395
−80	0.42	0.27	0.65	0.46	0.70	0.51	0.64	0.46
−90	0.47	0.31	0.75	0.54	0.82	0.60	0.75	0.54
−100	0.535	0.36			0.99	0.74	0.90	0.64

[a] Accuracy: ±0.01 cSt for ν; ±0.01 cP for η.

Table III. Self-Diffusion Coefficients, D, for Propene, Isobutene, *cis*- and *trans*-2-Butene, and Encounter Rate Constants, k_D, for Allylic Radicals Derived from These Compounds[a,b]

Temp, °C	Propene		Isobutene		*cis*-2-Butene		*trans*-2-Butene	
	D	$2k_D$	D	$2k_D$	D	$2k_D$	D	$2k_D$
0			6.2	40.4	5.6	37.2	6.2	40.4
−20			5.0	33.4	4.4	30.0	4.9	33.0
−40			3.8	26.2	3.5	24.4	3.8	26.4
−60	4.7	28.5	2.8	20.0	2.5	18.0	2.7	19.4
−80	3.4	21.3	1.9	13.8	1.7	12.6	1.9	13.8
−100	2.3	15.1	1.2	9.0	1.1	8.2	1.2	9.0
−120	1.4	9.5	0.66	5.0	0.59	4.4		
−140	0.74	5.1						

[a] D in units 10^{-5} cm² sec⁻¹. [b] k_D in units 10^9 M^{-1} sec⁻¹.

span and those beyond the reported range were estimated by extrapolation. The viscosity of liquid propene is reported at temperatures below −95°.[20] Values up to the boiling point can be estimated using the extrapolation formula suggested by Albright and Innes.[22] Since the viscosities of the butenes were not known, they were measured between −100° and their boiling points using a flow viscometer. The kinematic viscosities were converted to absolute viscosities. For calibration purposes the measurements were also carried out with propene. The values are slightly lower than those calculated by the extrapolation formula[21] but never deviate by more than 0.01 cP, indicating the accuracy of the extrapolation. The results of the viscosity measurements are given in Table II.

With viscosities and densities known, we calculated the encounter rate constants shown in Table III. In each case the calculated values of k_D fit the Arrhenius equation. The calculated effective activation energies are 1.17, 1.41, 1.45 and 1.39 kcal/mol for the radicals formed in propene, isobutene, *cis*-2-butene, and *trans*-2-butene, respectively.

The encounter rate constants should be compared with the rate constants for bimolecular decay of the allylic radicals at the limit of infinitely small peroxide concentrations. The observed increase in $2k_3$ with decreasing peroxide concentration could be due only partly to a change in the viscosity of the solution, since we have found that the addition of 0.27 and 0.55 M peroxide to propene or the butenes increased their liquid viscosities at −90° by only 10 and 24%, and near the boiling point by 9 and 18%, respectively. Since the increase in $2k_3$ shows little temperature dependence, it is probably not caused by reactions of the allylic radicals with the peroxide molecules but is more likely due to solvation of the radicals by the peroxide, thereby lowering their mobility. To approximate the rate constants $2k_3^0$ at infinitely small peroxide concentrations, the rate constants obtained with solutions containing 0.55 or 0.27 M peroxide were multiplied by factors derived from Figure 4 (1.9 and 1.3 for solutions containing 0.55 and 0.27 M peroxide, respectively). The Arrhenius plots of these rate constants for vanishing peroxide concentrations are given in Figures 5 and 6 and are compared with the calculated values of $2k_D$.

For allyl, 2-methallyl, and *trans*-1-methallyl radicals the activation energies derived from k_3 and k_D are the same within experimental error; the ratios k_D/k_3^0 are, respectively, 3.5, 4.0, and 4.5. We conclude that the rates of reaction are diffusion-controlled. The straightforward interpretation of the ratio, k_D/k_3^0, would be as a measure of the fraction of the diffusive encounters that result in reaction. The inefficiencies could be taken as indicative of the fact that the 75% of the encounters that would, on a statistical basis, lead to triplet radical pairs are unproductive. It is entirely possible that in solvents of such low viscosity the time for relaxation of triplets to singlets is longer than radical pair encounter times. This interpretation must be regarded with caution because of the dependence of the absolute values of k_D on the calculated values of gas-phase collision rates and the somewhat obscure relationship between details of collision processes in the gas phase and in solution.

The *cis*-1-methallyl radical shows different behavior. At −100° the ratio k_D/k_3^0 is 2.3, but at −30°, k_3 becomes equal to k_D. The more rapid increase in rate with increasing temperature is manifested in the higher appararent activation energy, 2.3 as compared with 1.4 for the activation energy for viscous flow. We see

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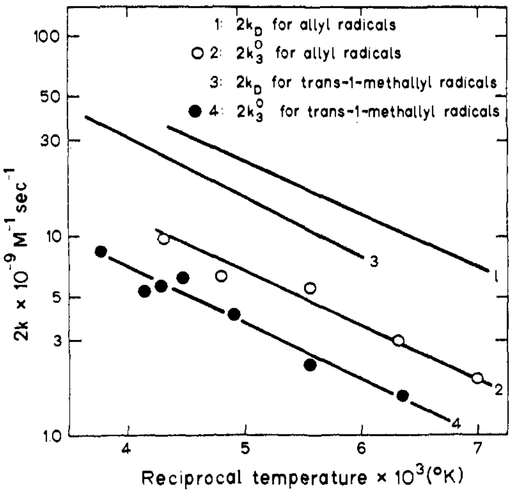

Figure 5. Comparison of encounter rate constants ($2k_D$) for allyl and *trans*-1-methallyl radicals with observed decay rate constants extrapolated to zero peroxide concentration ($2k_3^0$).

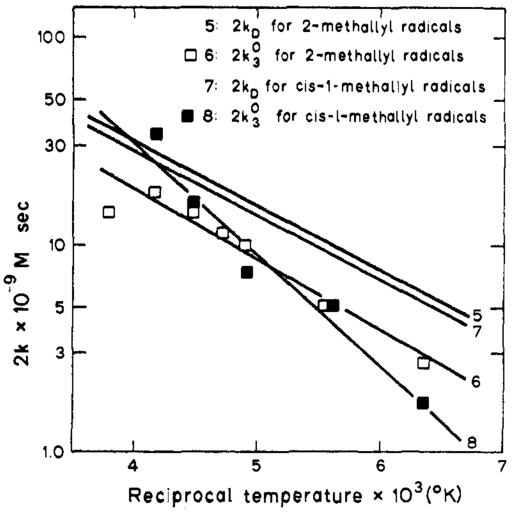

Figure 6. Comparison of encounter rate constants ($2k_D$) for *cis*-1-methallyl and 2-methallyl radicals with observed decay rate constants extrapolated to zero peroxide concentration ($2k_3^0$).

little merit in trying to attribute the difference in behavior between the cis and trans radicals to some extra activation barrier to radical coupling in the former case, since the rates are too fast rather than too slow. We believe that *cis*-1-methallyl radicals probably find some second path for decay. This path could be a first-order process since the rapid decay rates make testing of the second-order law impossible with this radical at the temperatures where the problems arise. The added decay reaction could be isomerization to the *trans*-1-methallyl radical. Halogenation studies at 80° show that considerable isomerization of allylic radicals can occur within a short lifetime and that, as would be expected, the trans radical is the more stable of the pair.[23] Furthermore, recent estimates of the resonance energy of the allylic radical indicate that the value is only 9.6 kcal/mol,[24] much lower than previously believed. One might posit that the potential barrier to isomerization is equal to the resonance energy of the radical, plus some small added barrier to rotation about a less than fully substituted single bond. Assuming an activation energy of 10–12 kcal/mol and a frequency factor of 10^{13} sec^{-1} leads to prediction of a rate constant of 10^2–10^4 sec^{-1} at −40°, rates that would be competitive with the bimolecular reaction rates at the radical concentrations produced in our experiments. However, Kochi and Krusic[2,3] did not observe cis–trans isomerization of the radicals at temperatures between 0 and −130°. The signals that we observed above −60° were too weak to apply the high resolution that would have been required to detect appearance of the trans radical in the experiments carried out in *cis*-2-butene. Alternative explanations could be found in postulating that the cis radical reacts rather rapidly with the parent hydrocarbon, or that the hydrocarbon contains some very reactive impurity. No significant impurity could be detected by glpc, so neither of these hypotheses appeals to us.

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