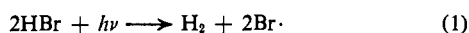# The Kinetics of the Photoaddition of Hydrogen Bromide to Propylene. Allyl Resonance Energy

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Abstract: The kinetics of the gas phase photohydrobromination of propylene have been investigated in the temperature range 51.5–150.0°, and at pressures between 18 and 185 Torr. For (HBr):(Pr) $\geqslant$ 1, and when the temperature is above 85°, the reaction rate expression was found to be: rate = $kI_0^{1/2}(CH_3CH=CH_2)^{1/2}(HBr)^2$. On the basis of these results a mechanism is proposed which includes the equilibrium $Br \cdot + CH_3CH=CH_2 \rightleftharpoons CH_2\dot{\cdots}CH\dot{\cdots}CH_2 + HBr$ and termination by combination of a bromine atom and an allyl radical. Interpretation of the experimental activation energy of −9.2 kcal/mol in terms of this mechanism leads to values of ΔH_f°(allyl) and the allyl resonance energy, respectively, of 41.5 ± 2 and 9.3 ± 2 kcal/mol.

The initial work on the gas phase photoaddition of HBr to small olefins was carried out by Vaughan, *et al.*[2] Their conclusion that the reaction proceeds by means of a radical chain mechanism has been accepted by all later workers. This mechanism may be written

$$2HBr + h\nu \longrightarrow H_2 + 2Br \cdot \quad (1)$$

$$Br \cdot + RCH=CH_2 \rightleftharpoons R\dot{C}HCH_2Br \text{ (I)} \quad (2, -2)$$

$$R\dot{C}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br \cdot \quad (3)$$

plus termination steps

where, depending upon the stability of I, all possible modes of termination have been proposed for the photohydrobromination of one olefin or another. Working with the addition of HBr to the 2-butenes and dideuterated ethylenes, Oldershaw and Cvetanović[3] demonstrated that reaction 2, −2, should actually be written

$$RCH=CH_2 + Br \cdot \rightleftharpoons R\dot{C}HCH_2Br^* \text{ (II)} \quad (4, -4)$$

$$R\dot{C}HCH_2Br^* + HBr \longrightarrow RCH_2CH_2Br + Br \cdot \quad (5)$$

$$R\dot{C}HCH_2Br^* + M \longrightarrow R\dot{C}HCH_2Br \text{ (I)} + M^* \quad (6)$$

as the initially formed bromoalkyl radical is vibrationally excited by the exothermicity of reaction 4. Field and Abell[4] found that the chemistry of the excited radical II must be considered in the photoaddition of HBr to ethylene at low pressures, but Wong and Armstrong[5] found that at higher pressures the chemistry of the thermal radical was dominant. Working at moderate pressures (50–200 Torr), however, Abell and coworkers have shown that the excited bromoalkyl radical need not be considered in the photohydrobromination of allene,[6] fluorinated ethylenes,[7] or in a competitive study of a series of olefins, all related to ethylene.[8] These results are understood in terms of reaction 6 (deactivation) being faster than either reaction −4 (decomposition) or 5 (propagation) for the excited radical II under these conditions. All of this work was interpreted in terms of propagation being carried out by the thermal

radical I. The present work was undertaken to explore more fully the relationship between the stability of the intermediate bromoalkyl radical and the kinetics observed, and to compare the actual thermodynamics of the photohydrobromination of propylene with those predicted from the data on ethylene[4] and the relative reactivity of ethylene and propylene toward HBr.[8]

Experimental Section

The HBr and propylene used were both Matheson Co. CP grade. Both were at least 98% pure to glpc and were thoroughly dried over phosphorus pentoxide and degassed at liquid nitrogen temperature before use.

Experiments were carried out in a seasoned cylindrical quartz cell (volume = 175 ml), housed in an insulated asbestos board oven, the temperature of which could be controlled to 0.02°. Irradiation was by means of a 100-W GE medium pressure quartz-jacketed mercury arc, with the Pyrex outer jacket removed. A Corning HR 954 filter was used to remove any light of wavelength below 2200 Å, and the light was collimated through the reaction cell with a quartz lens. The reaction cell was connected to an all-glass high vacuum line which was used to prepare and deliver reaction mixtures to it. Stopcocks in frequent contact with HBr were greased with Minnesota Mining and Manufacturing Kel-F 90 fluorocarbon grease, while the others were greased with Dow-Corning Silicone grease.

The reactants were either measured into the reaction cell individually using an optical lever system incorporated with a quartz spiral Bourdon gauge, or mixed to the desired proportions in a reservoir in the vacuum line, using mercury manometers, and then measured into the reaction cell using the Bourdon gauge. Selection of either mixing procedure produced the same kinetic results. The pressure of a mixture of reactants in the reaction cell remained constant in the dark overnight. Upon irradiation a small Draper effect was observed, and then the pressure decreased linearly with time until about 5% of the reactant present at the lower pressure was consumed. No reactions were allowed to proceed to greater than 10% completion, and most were held to under 5% completion. The slope of the time–pressure curve in this linear region was taken as the rate when the reactants were present at their initial pressures.

The light intensity exponent was determined by attenuation of the incident light beam by means of the insertion of calibrated neutral density filters into it. These were obtained from Oriel Optics Corporation, Stamford, Conn. As no actinometric work was done, no absolute rate constants were obtained in this work.

Results

Gas chromatographic analysis of the reaction mixture has shown that the only detectable products of the photohydrobromination of propylene (Pr) are the isomeric propyl bromides, with *n*-propyl bromide overwhelmingly predominating.[8] The over-all reaction is then $CH_3CH=CH_2 + HBr \rightarrow \alpha CH_3CH_2CH_2Br + (1$

(1) Address correspondence to: Department of Chemistry, University of Oregon, Eugene, Ore. 97403. Author to whom inquiries should be addressed.

(2) W. E. Vaughan, F. F. Rust, and R. E. Evans, *J. Org. Chem.*, **7**, 477 (1942).

(3) G. A. Oldershaw and R. J. Cvetanović, *J. Chem. Phys.*, **41**, 3639 (1964).

(4) R. J. Field and P. I. Abell, *Trans. Faraday Soc.*, **65**, 743 (1969).

(5) K. T. Wong and D. A. Armstrong, *Chem. Commun.*, 353 (1966).

(6) P. I. Abell and R. S. Anderson, *Tetrahedron Lett.*, 3727 (1964).

(7) G. J. Kavarnos and P. I. Abell, *Trans. Faraday Soc.*, in press.
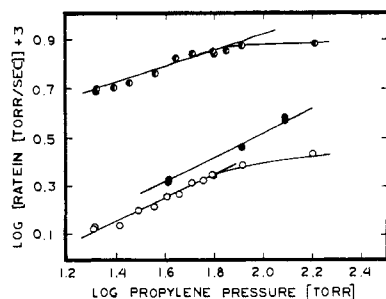
(8) P. I. Abell, *ibid.*, **60**, 2218 (1964).

Figure 1. Dependence of the rate of photoaddition on propylene pressure at constant I_0 and (HBr): ◑, temperature = 51.5°, HBr = 20.6 Torr, (HBr):(Pr) varies from 1 to $^1/_8$; O, temperature = 85.0°, HBr = 20.6 Torr, (HBr):(Pr) varies from 1 to $^1/_8$; and ●, temperature = 120.0°, HBr = 41.2 Torr, (HBr):(Pr) varies from 1 to $^1/_3$.
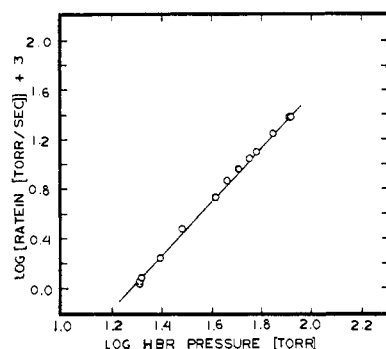

Figure 2. Dependence of the rate of photoaddition on HBr pressure at constant I_0 and propylene pressure; temperature = 85.0°, propylene = 20.6 Torr, (HBr):(Pr) varies from 1 to 4.

$-\alpha)(CH_3)_2CHBr$ and the rate of pressure decrease can be related to the over-all rate of production of propyl bromides, $d(PrBr)/dt$.

$$\text{rate} = \frac{d(PrBr)}{dt} = -\frac{dP}{dt}$$

For convenience in the discussion of these results only the intermediates leading to n-propyl bromide will be written, but it should be remembered that both bromides are produced.

The orders of the reaction in the three concentration variables were determined by measuring the rate at several pressures of a reactant while holding the concentrations of the other reactants constant. The log of the rate was then plotted against the log of the varied pressure and the slope of the plot taken as the order of the reaction in this reactant. Figure 1 shows such plots with the pressure of propylene varied while the concentration of HBr and the incident light intensity (I_0) were held constant. The slope of these plots, and hence the experimental order of the reaction in propylene, is a function of temperature and (HBr):(Pr). At the lowest temperature (51.5°) the propylene order is less than 0.25 at (HBr):(Pr) = 1, and approaches zero at lower values of this ratio. At the highest temperature (120.0°), however, the plot is linear with a slope of 0.5 throughout the (HBr):(Pr) range studied. At the intermediate temperature (85.0°) the observed order is 0.5 for values of (HBr):(Pr) close to 1, but falls at lower values of this ratio. This behavior demonstrates the complexity of the reaction, and in order to assure the observation of
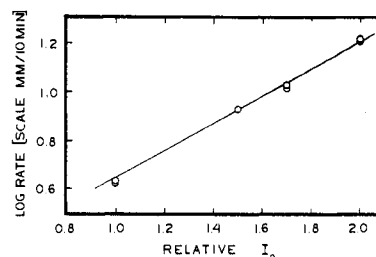

Figure 3. Dependence of the rate of photoaddition on I_0 with the pressures of HBr and propylene held constant; temperature = 85.0°, HBr = propylene = 9 Torr.
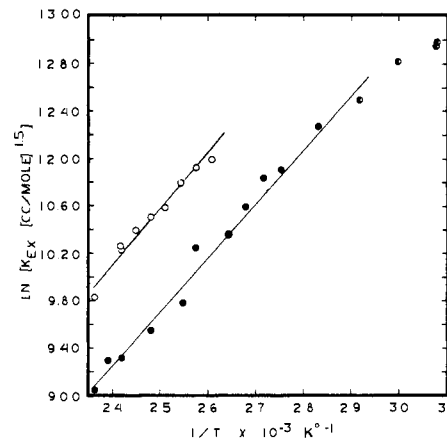

Figure 4. Arrhenius plots of k_{ex}; I_0 is held constant, HBr = propylene = 41.2 Torr.

clean kinetics, all further work was done at temperatures greater than 85.0° and at values of (HBr):(Pr) greater than 1.

Figure 2 shows the log (rate) vs. log (HBr) plot used to determine the order in HBr. The plot is linear over the range of HBr pressures studied and has a slope slightly above 2. The actual value is 2.1.

In Figure 3 log (rate) is shown plotted against the log of relative I_0. The highest I_0 was assigned a value of 100 and the relative values of the other intensities were calculated from the per cent transmittances of the neutral density filters used to attenuate the incident light beam. The order of the reaction in I_0 derived from this plot is 0.56. This value indicates that chain termination is carried out almost entirely by the gas phase combination of radicals. A perfect 0.50 is seldom found in long-chain radical reactions because some degree of termination usually takes place by the reaction of the chain carriers with impurities or at the wall of the reaction cell.

Combining the results of Figures 1-3 the most probable form of the experimental rate expression can be written as

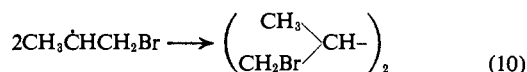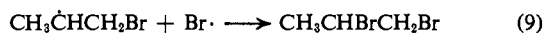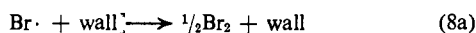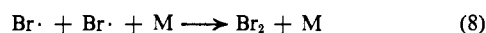$$\text{rate} = k_{ex}(Pr)^{1/2}(HBr)^2 \qquad (7)$$

$$k_{ex} = k_{ex}'I_0^{1/2}$$

This expression is valid only for (HBr):(Pr) $\geqslant$ 1 and when the temperature is greater than 85°.

Treating k_{ex} as a $^5/_2$-order rate constant, its value in concentration units ($cc^{1/2}/mol^{1/2}$ sec) was determined at several temperatures between 51.5 and 150.0°. I_0 was held constant in these runs and (HBr) = (Pr). These data are shown as an Arrhenius plot in Figure 4.
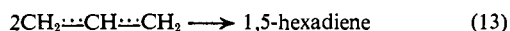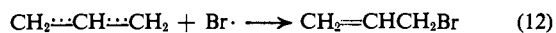
The plot is linear at temperatures above 85° and has a slope corresponding to an activation energy (E_{ex}) of -9.4 kcal/mol. At temperatures below 85° the slope of the Arrhenius plot falls, yielding less negative values of E_{ex}. This effect is assumed to be related to the change in propylene order seen in the same temperature range. An Arrhenius plot of values of k_{ex} obtained only between 100 and 150° is also shown in Figure 4. This plot is linear over the entire temperature range and has a slope corresponding to $E_{ex} = -9.0$ kcal/mol. The average of these two values of E_{ex} is -9.2 kcal/mol, and this will be taken as the experimental activation energy for the reaction in the region where eq 7 describes the kinetics. The difference in the intercepts of the two plots in Figure 4 is attributed to day to day variation in I_0.

Discussion

Proposed Mechanism. By analogy with the photohydrobromination of fluorinated ethylenes,[4-7] it was expected that the kinetics of the reaction with propylene could be interpreted in terms of reactions 1-3, coupled with one or more of the termination reactions 8-10, de-

$$Br\cdot + Br\cdot + M \longrightarrow Br_2 + M \tag{8}$$

$$Br\cdot + wall \longrightarrow {}^1\!/_2Br_2 + wall \tag{8a}$$

$$CH_3\dot{C}HCH_2Br + Br\cdot \longrightarrow CH_3CHBrCH_2Br \tag{9}$$

$$2CH_3\dot{C}HCH_2Br \longrightarrow \left(\begin{smallmatrix}CH_3\\CH_2Br\end{smallmatrix}\!\!>\!\!CH-\right)_2 \tag{10}$$

pending upon the stability of $R\dot{C}HCH_2Br$. However, no combination of assumptions could be devised by which a mechanism composed of these reactions generated a steady-state rate expression corresponding to the experimental (eq 7). The very negative value of E_{ex} seems to require termination by reaction 8, but this invariably leads to rate expressions involving (Pr) to the first power. Experimentally, the dependence of the reaction rate on (Pr) never rose above 0.5. It is known, however, that hydrogen atoms α to a double bond are abstracted by bromine radicals to give the corresponding allyl radical.[9,10] Under the assumption that this is occurring in the present case, another termination scheme can be proposed.

$$Br\cdot + CH_3CH{=}CH_2 \rightleftharpoons CH_2{\cdots}CH{\cdots}CH_2 + HBr \tag{11}$$

$$CH_2{\cdots}CH{\cdots}CH_2 + Br\cdot \longrightarrow CH_2{=}CHCH_2Br \tag{12}$$

$$2CH_2{\cdots}CH{\cdots}CH_2 \longrightarrow 1,5\text{-hexadiene} \tag{13}$$

Reaction 8 is not included as a possible termination step because it is a third-order reaction in competition with two second-order reactions and as such will not be important unless (Br·):(allyl) is very large. The one-half-order dependence of the rate on I_0 eliminates reaction 8a as a possible termination step. A steady-state treatment of reactions 1-3 and 11-13, assuming that both reactions 2 and 11 are at equilibrium, predicts the rate expression

$$\frac{d(PrBr)}{dt} = \frac{k_2 k_3}{K_{11}{}^{1/2}k_{-2}}\sqrt{\frac{k_1 I_0}{k_{12}(HBr) + K_{11}k_{13}(Pr)}} \times (Pr)^{1/2}(HBr)^{2.5} \tag{14}$$

If $k_{12}(HBr) \gg K_{11}k_{13}(Pr)$, then eq 14 becomes

(9) P. I. Abell, *J. Amer. Chem. Soc.*, **88**, 1346 (1966).
(10) A. Maccoll and R. A. Ross, *ibid.*, **87**, 1169 (1965).

$$\frac{d(PrBr)}{dt} = \frac{k_2 k_3}{K_{11}{}^{1/2}k_{-2}}\sqrt{\frac{k_1 I_0}{k_{12}}}(Pr)^{1/2}(HBr)^2 \tag{15}$$

which is identical in form with the experimental rate expression.

In this mechanism $K_2/K_{11} = (CH_3\dot{C}HCH_2Br)/(allyl)\cdot(HBr)$, and since reaction 2 is 8.5 kcal/mol exothermic, a large increase in $(CH_3\dot{C}HCH_2Br)/(allyl)$ is expected as the temperature is lowered. This would lead to increased termination by reactions 9 and 10. The observed kinetic changes to a lower dependence of the reaction rate on (Pr) and a less negative activation energy as the temperature is lowered are compatible with this viewpoint. $K_2(HBr)/K_{11}$ is estimated to be about 10^{-2} at 400°K, and (HBr) $= 100$ Torr.

Comparison of eq 7 and 15 leads to the relationship

$$k_{ex} = \frac{k_2 k_3}{K_{11}{}^{1/2}k_{-2}}\sqrt{\frac{k_1 I_0}{k_{12}}} \tag{16}$$

and interpretation of E_{ex} in terms of eq 16 can lead to a value of ΔH_{11}.

$$E_{ex} = E_2 + E_3 - E_{-2} - {}^1\!/_2\Delta E_{11} +$$
$$d(\ln(k_1 I_0))/dt = -9.2 \text{ kcal/mol} \tag{17}$$

It has been shown in these laboratories that $d(\ln(k_1 I_0))/dt$ is zero, and since reaction 12 is a radical combination reaction, $E_{12} = 0$. Abell[8] has shown that $(E_2' + E_3' - E_{-2}') - (E_2 + E_3 - E_{-2}) = 2.5$ kcal/mol, where the primed energies refer to the activation energies of reactions 2, -2, and 3 when ethylene is the olefin undergoing hydrobromination. From the work of Barker and Maccoll[11] and Field and Abell,[4] $(E_2' + E_3' - E_{-2}') = -6 \pm 1$ kcal/mol. Upon substitution of these figures into eq 17, the resulting value of ΔE_{11} is 1.4 ± 2 kcal/mol. As there is no change in the number of moles in reaction 11, $\Delta H_{11} = \Delta E_{11}$. The value of ΔH_{11} so obtained is assumed to be that at 125°, the midpoint of the Arrhenius plot. Using the thermodynamic data in Table I, $\Delta H_{11}°$ is calculated to be 1.3 $\pm$ 2 kcal/mol.

Table I. Summary of Thermodynamic Data for the Equilibrium
$Br\cdot + CH_3CH{=}CH_2 \rightleftharpoons CH_2{\cdots}CH{\cdots}CH_2 + HBr$

Material	$(\Delta H_f°)_g$, kcal/mol	$(S°)_g$, cal/deg mol	$C_p(25\text{-}125°)$, cal/deg mol
$CH_3CH{=}CH_2$	4.88[a]	63.80[d]	17.5[d]
$CH_2{\cdots}CH{\cdots}CH_2$	40.6[b]	63.4[e]	16.5[e]
HBr	-8.66[c]	47.43[e]	7.0[e]
$Br\cdot$	26.71[c]	41.81[c]	5.0[c]

[a] E. J. Prosen and F. B. Rossini, *J. Res. Natl. Bur. Stand.*, *A*, **36**, 269 (1946). [b] D. M. Golden, A. S. Rodgers, and S. W. Benson. *J. Amer. Chem. Soc.*, **88**, 3196 (1966). [c] "JANAF Thermochemical Tables," compiled and calculated by the Thermal Laboratory, Dow Chemical Co., Midland, Mich., 1960. [d] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940). [e] S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968, p 204.

This value of $\Delta H_{11}°$ can be used in conjunction with the data in Table I to calculate $\Delta H_f°(allyl)$.

$$\Delta H_f°(allyl) = \Delta H_{11}° - \Delta H_f°(HBr) +$$
$$\Delta H_f°(Br\cdot) + \Delta H_f°(Pr) = 41.5 \pm 2 \text{ kcal/mol}$$

(11) R. Barker and A. Maccoll, *J. Chem. Soc.*, 2839 (1963).

This value of $\Delta H_f°$(allyl) is in excellent agreement with values of the same quantity determined by Benson and coworkers of 40.6 ± 1 kcal/mol[12a] (later amended to 41.4 ± 1.1 kcal/mol)[12b] and 41.2 kcal/mol.[12c] The former of these values was determined from the thermal reaction of I_2 with propylene in the temperature range 208–300°, and the latter by the very low pressure pyrolysis (VLPP) of diallyl oxalate in the temperature range 913–1063°K. This agreement of the calculated value of $\Delta H_f°$(allyl) with that determined by Benson and coworkers, along with the agreement of theoretical and experimental rate expressions, is considered to be strong support for the proposed mechanism.

Evaluations of Assumptions Made. In the course of the derivation of eq 15 two assumptions were made which could be criticized. The first of these is that reaction 2 is at equilibrium. This implies that $k_{-2} \gg k_3$(HBr). However, it also has been claimed that $E_{-2} - E_3 = 8.5$ kcal/mol, i.e., reaction 3 is assumed to be slower than reaction -2, which has an activation energy 8.5 kcal/mol higher. The second questionable assumption is the exclusion of reaction 13 as a termination process.

Looking at these assumptions in order we first consider the relative rates of reactions -2 and 3 in terms of the expression

$$\text{relative rate} = k_{\text{rel}} = \frac{k_{-2}(CH_3\dot{C}HCH_2Br)}{k_3(CH_3\dot{C}HCH_2Br)(HBr)}$$

Substituting the "thermodynamic" forms of the rate constants we get

$$k_{\text{rel}} = \frac{A_{-2}\exp(-(E_{-2} - E_3)/RT)}{A_3(HBr)} \quad (18)$$

A_3 can be estimated from the reported values of A factors for similar metathetical radical-molecule reactions.[12a,13] It seems certain that $A_3 < 10^9$ l./mol sec. Few data seem to be available on the A factors for radical decomposition reactions such as reaction -2, but an estimate can be made from rough calculations of the entropy of activation, $\Delta S_{-2}^{\ddagger}$. This procedure has recently been reviewed by Benson.[14] The result of this calculation, giving the benefit of all doubt to a less positive value, is $\Delta S_{-2}^{\ddagger} \cong 1$ cal/mol deg. At 125°, A_2 is then equal to 10^{14} sec^{-1}. Placing these A factors into eq 18, and assuming the highest pressure of HBr used

in this work, 100 Torr, it is found that $k_{\text{rel}} > 200$. This calculation supports the assumption that reaction -2 is at equilibrium.

In a discussion of the assumption that reaction 12 is the dominant termination step it is convenient to define a quantity F, the fraction of termination carried out by reaction 12.

$$F = \frac{2k_{12}(\text{allyl})(\text{Br}\cdot)}{2k_{12}(\text{allyl})(\text{Br}\cdot) + k_{13}(\text{allyl})^2} \quad (19)$$

It has been pointed out that because of the greater loss of rotational degrees of freedom when two complex radicals combine, as compared to a radical-atom combination, it is expected that $10k_{13} \cong k_{12}$.[15] (Br·) and (allyl) can be related by means of K_{11},[125] which can be obtained from the experimental value of ΔH_{11}[125] and the value of ΔS_{11}[125] calculated from Table I. Hence ΔG_{11}[125] = -0.8 kcal/mol and K_{11}[125] = 2.7. Substitution of these quantities into eq 19 leads to the following values of (HBr): (Pr), F: 1:20, 0.25; 1:5, 0.60; 1:1, 0.90; 5:1, 0.98. These results indicate that at values of (HBr):(Pr) $\geqslant$ 1 the assumption that reaction 12 is the dominant termination step is probably valid. Because of the complexity of the kinetics observed under conditions of (HBr):(Pr) < 1, the proposed mechanism has already been limited to (HBr):(Pr) $\geqslant$ 1.

Allyl Resonance Energy (ARE). ARE may be defined as $DH_{25}°(CH_3CH_2CH_2-H) - DH_{25}°(CH_2=CHCH_2-H)$. From the value of $\Delta H_f°$(allyl) obtained in this work, $DH_{25}°(CH_2=CHCH_2-H)$ is found to be 88.7 ± 2 kcal/mol. The best value of $DH_{25}°(CH_3CH_2CH_2-H)$ is 98 ± 1 kcal/mol,[16] hence the value of ARE derived from our data is 9.3 ± 2 kcal/mol. Reported values of ARE run from 10 to 25 kcal/mol, but there now seems little doubt that the true value is in the range 10–14 kcal/mol. Benson and coworkers have reported values of ARE for the allyl radical itself of 10 ± 1.5 and 9.6 ± 1.5 kcal/mole.[12] The value reported here is well within the error limits of Benson's values, and in fact the agreement is remarkable.

While it now seems certain that ARE for the allyl radical itself is approximately 10 kcal/mol, reported values of ARE for substituted allyl radicals range from 12 to 14 kcal/mol.[12b,13c,17] This suggests that alkyl substitution may increase ARE by about 2 kcal/mol. In our system there seems to be good evidence that the true value of ARE for the allyl radical itself cannot be much more than 10 kcal/mol. If ARE were 12 kcal/mol, then ΔG_{11}[125] = -3.5 kcal/mol and K_{11}[125] = 75. For this value of K_{11}[125], $F = 0.21$ at (HBr):(Pr) = 1. We therefore would not expect to see termination by reaction 12 at values of (HBr):(Pr) < 25 unless $k_{12}/k_{13} \gg$ 10, which is not likely.

(12) (a) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966); (b) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); (c) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969).

(13) (a) A. F. Trotman-Dickenson, "Free Radicals," Methuen and Co., Ltd., London, 1959, p 65; (b) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968, p 100 (*A* factors of $10^{8.5}$ l./mol sec are suggested as being general for these reactions); (c) S. W. Benson, A. N. Bose, and P. N. Nangia, *J. Amer. Chem. Soc.*, **85**, 1388 (1963).

(14) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968, p 67.

(15) S. W. Benson, ref 14, p 154.

(16) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(17) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964); contains a review of reported values of ARE.