(14) At every temperature the calibration factor α_j in $I^j = \alpha_j k_e{}^j [j]_{ss}$, where j is m/e 67, 54 (1,5-hexadiene), and 44 (CO_2), was determined by at least two different flow rates $k_e{}^j[j]_{ss} = F_j{}^I$. α_j relates mass spectrometric intensities (I^j) to steady-state concentrations of a molecule ($[j]_{ss}$).

(15) $\ln (K_{r,d}/M^{-1}) = [\Delta S^\circ - \Delta n R(1 + \ln (R'T))]/R - \Delta E^\circ/RT$, where the superscript refers to a standard state of 1 atm and R' distinguishes the gas constant in units of L atm/mol K from units of cal/mol K.

(16) Defining $z_s = y_s k_e{}^{BA}(S)$, $z_B = y_B k_e{}^{BA}(B)$, and $K_{r,d} = k_r/k_d$, the propagation of errors yields for the relative error of $K_{r,d}$ the following expression:

$$\frac{\Delta K_{r,d}}{K_{r,d}} = \left(2\left(\frac{\Delta z_B + \Delta z_S}{z_B k_e{}^{BA}(B) - z_s k_e{}^{BA}(S)}\right)^2 + 2\left(\frac{\Delta z_B + \Delta z_S}{z_B - z_S}\right)^2 + \left(\frac{\Delta z_B}{z_B}\right)^2\right)^{1/2}$$

(17) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

(18) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 217 (1969).

(19) The uncertainty in ΔH° from the equilibrium measurements (2) is estimated to be ±1 kcal/mol. Together with the uncertainty in ΔH°_f(BA) of ±0.5 kcal/mol, the combined uncertainty for ΔH°_f(allyl,g) amounts to ±1.5 kcal/mol.

(20) M. Rossi and D. M. Golden, *J. Am. Chem. Soc.*, following paper in this issue.

(21) K. Y. Choo, P. C. Beadle, L. W. Piszkiewicz, and D. M. Golden, *Int. J. Chem. Kinet.*, **8**, 45 (1976).

(22) $I^{N_2} = \alpha_{N_2} k_e{}^{N_2}[N_2]_{ss} = \alpha_{N_2} F^0{}_{N_2} = \alpha_{N_2} F^I{}_{N_2}$. For explanation of symbols, see ref 14.

(23) Experiment no. 1 in Table III was performed at an earlier stage of the recombination series than no. 2 and 3, indicating variable wall conditions of the reaction vessel within the series of experiments.

(24) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, 1972.

(25) (a) G. P. Smith, M. Lev-On, and D. M. Golden, submitted for publication; (b) A. C. Baldwin and D. M. Golden, *J. Phys. Chem.*, **82**, 644 (1978); (c) A. C. Baldwin, K. E. Lewis, and D. M. Golden, *Int. J. Chem. Kinet.*, submitted.

(26) The separation distance along the bond axis was chosen in such a way that it corresponded to the top of the centrifugal barrier in a model for a Lennard–Jones potential of the C–C bond connecting both C_3H_5 units: $\rho^+ = r^+/r_0 = (6D_0/RT)^{1/6}$. This rotational maximum of the effective potential, including rotation, is not very sensitive to either T or the precise value of D_0, and for most common values of both occurs in the range $\rho^+ = 2.5$–3.0.

(27) For any reaction

$$AB \underset{r}{\overset{d}{\rightleftarrows}} A + B$$

$$\Delta E^\circ{}_0 = E^\circ{}_d - E^\circ{}_r \equiv E^\circ{}_d = \Delta E^\ddagger{}_{o,d} \equiv \text{critical energy}$$
$$E^T{}_d \equiv \Delta E^\ddagger{}_{T,d} + RT = \Delta E^\ddagger{}_{o,d} + \langle \Delta C^\ddagger{}_{v,d} \rangle^T{}_0 T + RT$$
$$E^T{}_d = \Delta E^\circ{}_0 + \langle \Delta C^\ddagger{}_{v,d} \rangle^T{}_0 T + RT$$

since

$$\Delta E^\circ{}_0 = \Delta E^\circ{}_T - \langle \Delta C_v \rangle^T{}_0 T$$
$$E^T{}_d = \Delta E^\circ{}_T - \langle \Delta C_v \rangle^T{}_0 T + \langle \Delta C^\ddagger{}_{v,d} \rangle^T{}_0 T + RT$$
$$E^T{}_d = \Delta H^\circ{}_T + \langle \Delta C^\ddagger{}_{v,r} \rangle^T{}_0 T$$

(28) Given η and $I_A I_B I_C$ for a rotational model transition state, changing $I_A I_B I_C$ to $I_A' I_B' I_C'$ results in a different hindrance parameter (η') to yield the same Arrhenius A factor through the following relation:

$$\eta' = 100 - (100 - \eta)\left(\frac{I_A' I_B' I_C'}{I_A I_B I_C}\right)$$

If $I_A' I_B' I_C' > I_A I_B I_C$, it then follows that $\eta' < \eta$.

(29) W. L. Hase, *J. Chem. Phys.*, **64**, 2442 (1975); W. L. Hase in "Dynamics of Molecular Collisions", W. H. Miller, Ed., Plenum Press, New York, 1976.

(30) $k_r(\exp) = A_r e^{-3.3/2}$ at $T = 1000$ K with $E_r = 3.3$ kcal/mol from $E_d = 59.3$ kcal/mol, and $\Delta E = 56.0$ kcal/mol.

(31) See references in ref 22a; S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 21** (1970).

(32) G. McKay and I. M. C. Turner, *Int. J. Chem. Kinet.*, **10**, 89 (1978).

(33) D. A. Parkes and C. R. Quinn, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1952 (1976).

Absolute Rate Constants for Metathesis Reactions of Allyl and Benzyl Radicals with HI (DI). Heat of Formation of Allyl and Benzyl Radicals

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Abstract: The metathesis reaction $C_3H_5\cdot + HI\ (DI) \rightarrow C_3H_6\ (C_3H_5D) + I\cdot$ (k_3) has been studied in the gas phase using the VLPP technique. The result with DI, using diallyl oxalate as a radical source, is $\log (k_3{}^D/M^{-1}\,s^{-1}) = (10.11 \pm 0.30) - (5.7 \pm 1.5)/\theta$ at $T = 1000$ K. The result using 3,3′-azopropene as a radical source is $\log (k_3/M^{-1}\,s^{-1}) = 8.93 \pm 0.18$ at $T = 1000$ K, where $\theta = 2.303RT$ in kcal mol^{-1}. For the metathesis reaction $C_6H_5CH_2\cdot + DI \rightarrow C_6H_5CH_2D + I\cdot$ (k_3), $\log (k_3{}^D/M^{-1}\,s^{-1}) = (10.46 \pm 0.30) - (6.3 \pm 1.5)/\theta$ at $T = 1000$ K. These rate expressions were extrapolated to lower temperatures using a transition-state model in order to compute the equilibrium constants for the above metathesis reactions using the rate constants for the reverse metathesis from iodination studies. The equilibrium constants yield $\Delta H^\circ{}_f$(allyl) = 39.4 ± 1.5 kcal/mol and $\Delta H^\circ{}_f$(benzyl) = 47.80 ± 1.5 kcal/mol at $T = 300$ K. These values correspond to stabilization energies of 11.4 ± 1.5 and 10.1 ± 2.0 kcal/mol, respectively (i.e., DH(allyl–H) = 86.6 ± 1.5 kcal/mol and DH($C_6H_5CH_2$–H) = 87.9 ± 1.5 kcal/mol).

I. Introduction

A large number of values for free-radical heats of formation ($\Delta H^\circ{}_f$ (R·)) have been obtained by the spectrophotometric iodination technique which is well documented in the literature.[1]

The pertinent reactions are

$$I_2 + M \rightleftarrows 2I\cdot + M \quad K_{12} \tag{1}$$

$$RI + I\cdot \underset{k_2}{\overset{k_1}{\rightleftarrows}} R\cdot + I_2 \quad K_{1,2} = k_1/k_2 \tag{2}$$

$$R\cdot + HI \underset{k_4}{\overset{k_3}{\rightleftarrows}} RH + I\cdot \quad K_{3,4} = k_3/k_4 \tag{3}$$

with the following overall equilibrium:

$$RI + HI \rightleftarrows RH + I_2 \tag{4}$$

In general, the temperature-dependent values of k_1 and k_2/k_3 (starting with RI + HI) or k_4 and $K_{3,4}$ (starting with RH + I_2) can be obtained. The usual method of extracting $\Delta H^\circ{}_f$(R·) from these studies is to assume that $E_2 = 0.0 \pm 1.0$ kcal/mol and/or $E_3 = 1.0 \pm 1.0$ kcal/mol. (The measured values of $E_2 - E_3$ are not inconsistent with these assumptions). Thus, a measurement of E_4 will yield a value for $\Delta H^\circ{}_{3,4}$ and $\Delta H^\circ{}_f$(R·) will follow since the appropriate values for HI, I· and RH are known.[2]

Very low-pressure pyrolysis (VLPP) allows the measurement of fast bimolecular reactions such as (5) in the gas phase.

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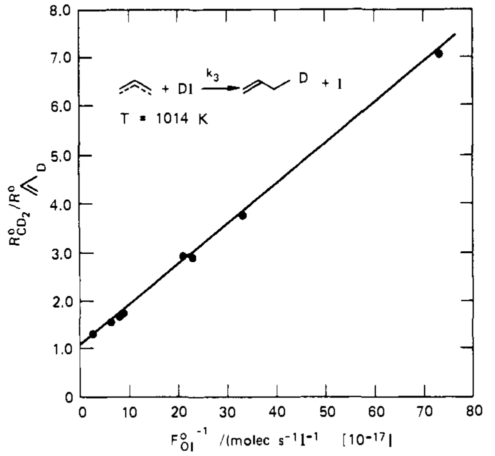


Figure 1. Experimental determination of k_3 (see eq 8) for the metathesis reaction allyl· + DI → propylene-d_1 + I· at 1014 K. Representative example from Table I.

$$R\cdot + HI \xrightarrow{k_3} RH + I\cdot \quad (5)$$

We take advantage of the fact that the measured rate constants k_3 are unencumbered by competitive radical-radical recombinations relative to which the overwhelming majority of fast bimolecular radical-molecule reactions have been measured.[3] The availability of Arrhenius parameters for forward and back reaction rate constants provides values for $\Delta H^\circ_f(R\cdot)$ and entropies of radicals ($S^\circ(R\cdot)$). Accordingly, we report in this work the rates of the reactions

$$C_3H_5\cdot + HI\ (DI) \xrightarrow{k_3} C_3H_6\ (C_3H_5D) + I\cdot \quad (6)$$

$$C_6H_5\dot{C}H_2 + HI\ (DI) \xrightarrow{k_3} C_6H_5CH_3\ (C_6H_5CH_2D) + I\cdot \quad (7)$$

together with their Arrhenius parameters over an extended temperature range, thereby obtaining values for $\Delta H^\circ_f(R\cdot)$ of allyl ($C_3H_5\cdot$) and benzyl ($C_6H_5\dot{C}H_2$) radicals by using the results of previously published determinations of k_4, A_4, and E_4 from iodination studies of propylene[4] and toluene.[5]

II. Experimental Section

The description of the VLPP molecular beam sampling apparatus, together with the all-quartz reaction vessel (Knudsen cell), has been presented in the preceding publication.[6] The two-aperture Knudsen cell was characterized by the following parameters: $V = 0.134$ L, $\omega = 4982(T/M)^{1/2}$ s^{-1}, $k_e^M(B) = 2.5571(T/M)^{1/2}$ s^{-1}, $k_e^M(S) = 0.2088(T/M)^{1/2}$ s^{-1}, B referring to the large and S to the small reactor escape aperture. The source and purification of the radical precursors diallyl oxalate ($C_8H_{10}O_4$), 3,3′-azo-1-propene ($C_6H_{10}N_2$), and bibenzyl ($C_{14}H_{14}$) have also been described.[6] Benzyl vinyl ether ($C_9H_{10}O$) was synthesized according to literature methods.[7] GC-MS analysis showed a 2% impurity of benzaldehyde (C_7H_6O), which did not interfere with our measurements. The standard gas-handling system was heated in order to increase the vapor pressure of diallyl oxalate, bibenzyl, and benzyl vinyl ether, such that suitable flow rates of the radical precursors into the heated Knudsen cell could be obtained. Hydrogen iodide (Linde Air Products, Inc.) and deuterium iodide (99 atom %, Merck Sharp and Dohme, Ltd., Canada) were used without further purification. The experiments were carried out by setting the flow of the radical precursor to a low and constant value and monitoring m/e 43 (C_3H_5D) and 92 (C_7H_8) or 93 (C_7H_7D) as a function of flow rate of HI or DI. The reaction vessel had two inlet (capillary or needle valve) systems from two independent gas-handling systems so that the components met for the first time in the hot reactor.

III. Results and Discussion

A. Allyl Radical + HI (DI). Diallyl oxalate ($C_8H_{10}O_4$) was used as a precursor for allyl radicals at ⟨T⟩ = 1000 K and 3,3′-azo-1-propene ($C_6H_{10}N_2$) at ⟨T⟩ = 750 K. By using two different precursors for allyl radical it was possible to cover a range of 380 K in the study of the metathesis (6). Application of the steady-state assumption to reaction 6 in a low-pressure stirred flow reactor results in the following relation[8] (see Appendix for details of the derivation):

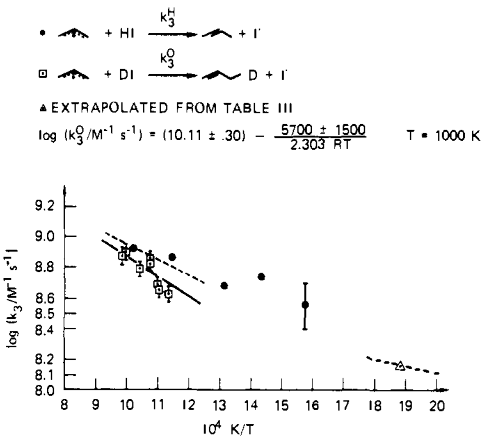


Figure 2. Arrhenius plot of rate constants from Table I: —, least squares analysis of Arrhenius plot with rate constants k_3^D for the reaction $C_3H_5\cdot$ + DI → C_3H_5D + I·; - - -, predicted rate constants k_3^H for the reaction $C_3H_5\cdot$ + HI → C_3H_6 + I· taking into account the primary isotope effect when DI is replaced by HI.

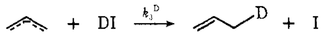
$$1/f = 1 + \frac{k_e^{C_3H_5\cdot}k_e^{HI}}{k_3 R^i_{HI}} = 1 + \frac{k_e^{C_3H_5}}{k_3(HI)} \quad (8)$$

where f is the fraction of radicals "titrated" at a certain steady-state concentration (HI)/M or specific flow of HI into the reactor (R^i_{HI}/molecules s^{-1} L^{-1}), and $k_e^{C_3H_5\cdot}$ and k_e^{HI} are the escape rate constants (s^{-1}) of allyl radical and HI out of the reactor. f is defined as $(C_3H_6)/(C_3H_6)_\infty$, where (C_3H_6) is the steady-state concentration of C_3H_6 at a certain (HI), and $(C_3H_6)_\infty$ is the same concentration at (HI) = ∞, where essentially all radicals have reacted with HI. In the case of diallyl oxalate as precursor for allyl radical, (CO_2) could be taken as representative of the amount of the allyl radicals present in the reaction system, so that $1/f$ could be equated to $(CO_2)/(C_3H_6)$ or $R^\circ_{CO_2}/R^\circ_{C_3H_6}$. This method proved to be valid because plots of $1/f$ vs. $R^\circ_{CO_2}/R^\circ_{C_3H_6}$ yielded straight lines with unit intercepts, confirming that the amount of CO_2 present was indeed representative of the amount of allyl radical in the system. We believe that use of CO_2 as a marker for the production of allyl radicals in the system diallyl oxalate + DI renders the determination of the rate constant k_3^D more reliable than k_3^H for the system 3,3′-azo-(1)-propene + HI, where the contribution of N_2 had to be evaluated by subtraction of mass spectrometric signals at m/e 28. The following assumptions have been made in deriving eq 8: (HI) ≫ ($C_3H_5\cdot$) and $R^i_{HI} = R^\circ_{HI}$, where R^i_{HI} is the flow of HI in and R°_{HI} is the flow out of the reactor. Under our experimental conditions both assumptions were found to be justified, so that a plot of $1/f$ vs. $1/(R^i_{HI})$ gave a straight line with unit intercept (within experimental error) and $(k_e^{C_3H_5\cdot}k_e^{HI})/k_3$ as slope, from which k_3 was readily obtained, given the reactor parameters.[6] Special attention was paid to the requirement of carrying out the titration at the lowest possible concentration of $C_3H_5\cdot$ in order to suppress the bimolecular recombination reaction. Figure 1 displays a typical plot of $1/f$ vs. $1/(F^i_{DI})$ and Table I lists the rate constants k_3/M^{-1} s^{-1} as a function of temperature. These are plotted in the usual Arrhenius form in Figure 2. The results from Table I are

$$k_3^D = 7.2 \times 10^8\ M^{-1}\ s^{-1} \text{ at } \langle T \rangle = 1000\ K$$

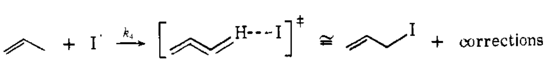
$$k_3^H = 3.6 \times 10^8\ M^{-1}\ s^{-1} \text{ at } T = 635\ K$$

Table I. Rate Constants for Metathesis Reactions as a Function of Temperature

T, K	$k_3/M^{-1}\ s^{-1}$
	
884	4.30×10^8 [a]
907	4.80×10^8 [a]
911	4.90×10^8 [a]
929	6.68×10^8 [a]
929	6.99×10^8 [a]
962	6.37×10^8 [a]
1007	8.06×10^8 [a]
1014	6.76×10^8 [a]
	
635	3.57×10^8 [b,c]
697	5.50×10^8 [b]
761	4.83×10^8 [b]
878	7.24×10^8 [b]
982	8.54×10^8 [b]

[a] Radical source: diallyl oxalate ($C_8H_{10}O_4$). [b] Radical source: 3,3′-azo-1-propene ($C_3H_5N_2C_3H_5$). [c] Average value of three experiments.

Table II. Estimated Entropy of Activation for the Metathesis Reaction $C_3H_6 + I\cdot \rightarrow C_3H_5\cdot + HI$ (Standard State: 1 atm)



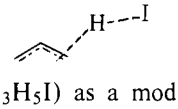
$$\Delta S_4^{0\ddagger'} = S^0(C_3H_5I) - S^0(I\cdot) - S^0(C_3H_6)$$

	300 K	530 K	1000 K
$\Delta S_4^{0\ddagger'}$	−28.42	−29.30	−30.56
corrections:			
spin (R ln 2)	1.39	1.39	1.39
rotation[a]	2.11	2.11	2.11
2 bending (C···H···I): 300 cm⁻¹	2 × 1.40	2 × 2.40	2 × 3.60
1 stretch (C···H···I)	reaction coordinate		
resonance stiffening of internal rotation $V_0 = 2 \rightarrow 13$ kcal/mol	−2.30	−2.10	−1.67
C=C, 1650 cm⁻¹ → C—C, 1400 cm⁻¹	0.0	0.0	+0.10
C—C, 1000 cm⁻¹ → C—C, 1400 cm⁻¹	−0.10	−0.30	−0.50
420 cm⁻¹ → 635 cm⁻¹	−0.52	−1.00	−0.90
$\Delta S_4^{0\ddagger}$	−25.04	−24.40	−22.63

[a] Adjusted to give experimental A_4 at $\langle T\rangle = 530$ K log $(A_4/M^{-1}\ s^{-1}) = 10.25$.

Owing to the better quality of the DI data compared to the HI data (smaller uncertainty limits, pure sample, more points over a certain temperature range (see above)), the following approach was taken in this paper. The Arrhenius expression for the DI data, given by log $k_3^D/M^{-1}\ s^{-1} = (10.11 \pm 0.30) - (5.7 \pm 1.5)/\theta$ at $T = 1000$ K, where $\theta = 2.303RT$ in kcal/mol, was transformed to an Arrhenius expression for the HI data by means of the experimentally derived ratio $k_3^H/k_3^D = 1.18$ at $T = 1000$ K (Figure 2). The isotope effect was accounted for by setting $A_3^D/A_3^H = 1.26$ and choosing $E_3^D - E_3^H = 0.80$ kcal/mol, so that $k_3^H/k_3^D = 1.18$, resulting in the following Arrhenius expression for the HI system: log $(k_3^H/M^{-1}\ s^{-1}) = (10.01 \pm 0.30) - (4.9 \pm 1.5)/\theta$ at 1000 K. This small isotope effect is in line with expectations from an extensive body of data, indicating $k^H/k^D = 1.5 \pm 0.5$[9] at temperatures around 500 K. The data for the HI system (Figure 2) suggest slight curvature of the corresponding Arrhenius plot. In the following paragraph a transition state model for reaction 6 or its reverse (with HI as reagent) will be developed, which will result in temperature-dependent Arrhenius parameters and therefore will be compatible with a curved Arrhenius plot of k_3^H.

Golden et al.[4] found the following rate expression at $\langle T\rangle = 530$ K: log $(k_4/M^{-1}\ s^{-1}) = 10.25 - 18.04/\theta$, where $\theta = 2.303RT$ in kcal mol⁻¹. In order to provide a value at 1000 K for the equilibrium constant $K_{4,3} = k_4/k_3$ (3), where $R\cdot = C_3H_5\cdot$, a transition-state model, which has been shown by Benson and co-workers to be appropriate[2] in cases of metathesis reactions, such as (6) and (7), was used to extrapolate the measured rate constant k_4 from 530 to 1000 K. The transition state (9) for reaction 6 or its reverse was approximated by



(9)

taking allyl iodide (C_3H_5I) as a model, adding two CHI bending and one (CH)-I stretching (= reaction coordinate) mode to C_3H_5I, and including other minor corrections due to the presence of the extra H atom in (9). Table II demonstrates the method and summarizes the result for the entropy of activation $\Delta S_4^{0\ddagger}$ of the reverse of reaction 6. Using the $\langle \Delta C^{\ddagger}_{p,4}\rangle$ value listed in Table III and the relation

$$\Delta E_c = \Delta T\langle \Delta C_p^{\ddagger}\rangle_{T_1}^{T_2} + 2R\Delta T, \quad \Delta T = T_2 - T_1 \quad (10)$$

for the change in Arrhenius activation energies of rate constants expressed in molar units (M) one obtains the following Arrhenius expression for k_4 at $T = 1000$ K: log $(k_4/M^{-1}\ s^{-1}) = 11.15 - 21.22/\theta$ (see Table III, column 3). $K_{4,3}$ at $T = 1000$ K then turns out to be 3.98×10^{-3}, which, together with an estimate for $S°$(allyl)[10] and C_p data[2,10] (Table III, column 7), yields a "third law" standard heat of formation $\Delta H°_f$(allyl) = 39.4 ± 1.5 kcal/mol at $T = 300$ K.[14] Table III, column 3, also shows the Arrhenius expression for k_4 at 300 K deduced as before by means of $\langle \Delta C^{\ddagger}_{p,4}\rangle$. Furthermore, the Arrhenius expression for k_3 was extrapolated to lower temperature (see Table III, column 2) with $\Delta S_4^{0\ddagger}$, and the estimated overall entropy change $\Delta S°_{4,3}$ for reaction 6[2] resulting in an Arrhenius activation energy of 2.1 kcal/mol for k_3 at $T = 530$ K, a value slightly different from the "usual" assumed value of 1.0 ± 1.0 kcal/mol used throughout the literature.[1] Table III thus provides a good example of an internally consistent set of Arrhenius and thermochemical parameters.

The allyl radical heat of formation derived above from two separate experiments is in excellent agreement with a recent equilibrium study and other determinations of $\Delta H°_f$(allyl).[6] The present value for $\Delta H°_f$(allyl) provides an allyl resonance stabilization energy (ARE) of 11.4 ± 1.5 kcal/mol (see, e.g., ref 11 for the definition of ARE). The large variation of A_3 and A_4 with temperature (Table III) is noteworthy; this brings about a concomitant change in E_3 and E_4 which tends to partially cancel the increase in the A factor. Obviously, this cancellation of log A vs. E is only partial, so that the suggested slight curvature in the Arrhenius plot in Figure 2 results. It has repeatedly been pointed out in the literature[3] that the Arrhenius A factor for the reaction of I· with an alkane or olefin is quite high (log $A_4 = 10.3$ at 550 K). Such a behavior is obvious from Table III in the present case as well.

B. Benzyl Radical + HI (DI). At $\langle T\rangle = 880$ K benzyl radicals were generated by unimolecular decomposition of benzyl vinyl ether (C_7H_7-OC_2H_3) and at $\langle T\rangle = 1060$ K by the bond-breaking process in bibenzyl (C_7H_7-C_7H_7). The evaluation of the rate constant k_3 (7) follows the same lines as in the case of allyl radical. Figure 3 displays a typical $1/f$ vs. $1/(F_{DI})$ plot (eq 8), where f represents, by analogy with the definition given in section A, the fraction of radicals titrated at a certain steady-state concentration of HI with respect to the total concentration of radicals present in the absence of HI; Table IV lists the resulting rate constants $k_3/M^{-1}\ s^{-1}$ as a function of temperature, and Figure 4 shows the corresponding Arrhenius plot. By using two different benzyl radical precur-

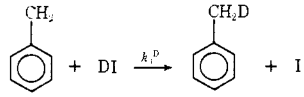
Table III. Kinetic and Thermochemical Parameters for the Equilibrium[e]

$$\text{propylene} + \text{I}\cdot \underset{k_3}{\overset{k_4}{\rightleftarrows}} \text{allyl}\cdot + \text{HI}$$

T/K	log (k_3/M^{-1} s^{-1})	log (k_4/M^{-1} s^{-1})	$\Delta S°_{4,3}$,[a] eu	$\Delta S°_{4,3}$,[b] eu	$\Delta H°_{4,3}$, kcal mol^{-1}	$\langle \Delta C_{p4,3} \rangle$	$\langle \Delta C^{\ddagger}_{p4} \rangle$[d]
1000	log k_3^D *10.11 − 5.7/θ*						
1000	log k_3^H 10.01 − 4.9/θ	11.15 − 21.22/θ	5.25	5.94	16.30		
						0.85	2.79
530	9.03 − 2.12/θ	*10.25 − 18.04/θ*	5.62	5.40	15.90		
						1.60	1.12
300	8.59 − 1.31/θ	9.60 − 16.86/θ	4.65	4.50	15.53[c]		

[a] From Arrhenius expressions using $\ln (A_4/A_3) = \Delta S°_{4,3}/R$. [b] Thermochemical estimate, ref 2 and 10. [c] Yields $\Delta H°_f$(allyl) = 39.40 ± 1.50 kcal/mol at 300K. [d] Calculated from $\Delta S_4°^{\ddagger}$ of transition-state model in Table II. [e] Italicized values represent experimental results; others are extrapolated Arrhenius parameters using transition-state model (9) from Table II ($\theta = 2.303RT$ in kcal/mol), and estimated values for $\Delta S°_{4,3}$ (column 5 of Table III).

Table IV. Rate Constants for the Metathesis Reaction as a Function of Temperature



T/K	k_3/M^{-1} s^{-1}	T/K	k_3/M^{-1} s^{-1}
811	7.08×10^8 [a]	1038	1.51×10^9 [b]
851	5.78×10^8 [a]	1049	1.27×10^9 [b]
856	9.03×10^8 [a]	1050	1.70×10^9 [b]
922	6.99×10^8 [a]	1088	1.37×10^9 [b]
963	9.35×10^8 [a]	1090	1.32×10^9 [b]
986	1.35×10^9 [b]	1109	1.72×10^9 [b]
1004	1.23×10^9 [b]	1126	2.30×10^9 [b]
1007	1.40×10^9 [b]		

[a] Radical source: benzyl vinyl ether ($C_6H_5CH_2OC_2H_3$). [b] Radical source: bibenzyl (1,2-diphenylethane).

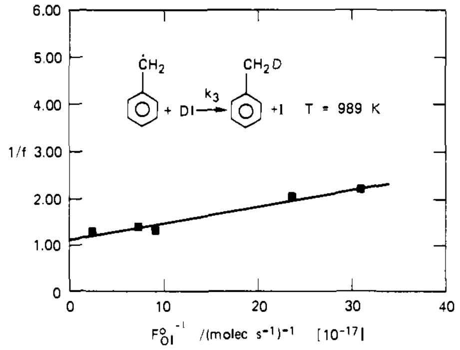


Figure 3. Experimental determination of k_3 (see eq A-10) for the metathesis reaction benzyl· + DI → toluene-d_1 + I· at 989 K. Representative example from Table IV.

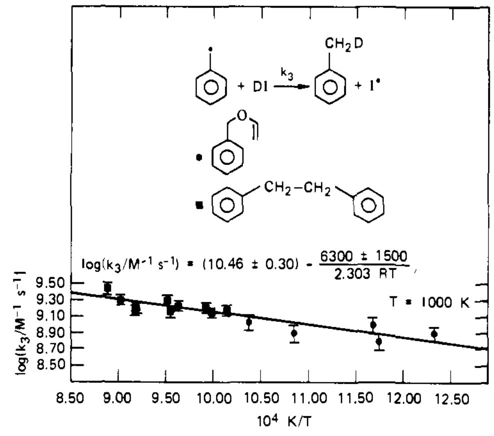
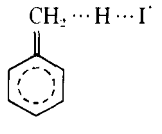


Figure 4. Least-squares Arrhenius plot of rate constants from Table IV for the reaction $C_7H_7\cdot$ + DI → C_7H_7D + I·: ■, bibenzyl as precursor; ● benzyl vinyl ether as precursor for benzyl radicals.

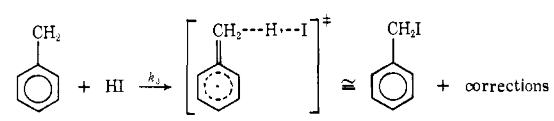
sors, which decompose at different temperatures, it was possible to study the metathesis reaction 7 over a range of 315 K.

The rate constant k_3^D was found to be 1.23×10^9 M^{-1} s^{-1} at $\langle T \rangle$ = 1000 K. The activation energy E_3^D at 1000 K is 6.3 ± 1.5 kcal/mol as found by a least-squares analysis log (A_3^D/M^{-1} s^{-1}) = 10.46 ± 0.30), in remarkable agreement with the parameters found for allyl radical. The Arrhenius plot in Figure 4 suggests, by analogy with the allyl case, slight curvature at higher temperatures and a possible small systematic error between the two series of different precursors for benzyl radical, but it is obvious as well that the straight line, corresponding to E_3 = 6.3 ± 1.5 kcal/mol, does not do violence to the present data. In close analogy to the allyl case discussed in part A, the experimental Arrhenius expression for k_3^D at 1000 K was transformed into an Arrhenius expression for k_3^H to account for the primary isotope effect, replacing DI by HI as reagent. The result is log (k_3/M^{-1} s^{-1}) = (10.36 ± 0.30) − (5.5 ± 1.5)/θ, where $\theta = 2.303RT$ in kcal/mol, and the condition k_3^H/k_3^D = 1.18, as measured experimentally in the allyl case, holds. Owing to the more preliminary nature of the iodination study of toluene,[5] the experimental rate of the reverse of reaction 7 at T = 500 K was assumed to be correct (1.41×10^2 M^{-1} s^{-1}) rather than using the published Arrhenius parameters, since A_4/M^{-1} s^{-1} seems to be too low by at least two orders of magnitude (log (A_4/M^{-1} s^{-1}) = 8.75, E_4 = 15.20 kcal/mol). In order to derive a value for the equilibrium constant $K_{4,3} = k_4/k_3$ at T = 500 K (3), where R· = $C_7H_7\cdot$, the transition-state model (11) was used by analogy with the allyl case, discussed above. Benzyl iodide (C_7H_7I) was taken as a model and corrected for the transition state (10) as before. Table V shows the detailed corrections and the computed entropy of activation $\Delta S_3°^{\ddagger}$ for reaction 7. Using the $\langle \Delta C^{\ddagger}_{p,3} \rangle$ value listed in Table VI, as computed from the temperature-dependent $\Delta S_3°^{\ddagger}$ values of Table V and relation 10 for the change in Arrhenius activation energy with temperature, one obtains the following Arrhenius expression for



(11)

Table V. Estimated Entropy of Activation for the Metathesis Reaction $C_7H_7\cdot + HI \rightarrow C_7H_8H + I\cdot$ (Standard State: 1 atm)



$$\Delta S_3^{0\ddagger'} = S^0(C_7H_7I) - S^0(HI) - S^0(C_7H_7\cdot)$$

	300 K	500 K	1000 K
$\Delta S_3^{\circ\ddagger'}$	−33.23	−35.22	−37.44
corrections:			
spin (R ln 2)	1.39	1.39	1.39
rotation[a]	2.94	2:94	2.94
2 bending (C$\cdots$H$\cdots$I): 200 cm^{-1}	2 × 2.20	2 × 3.10	2 × 4.40
1 stretch (C$\cdots$H$\cdots$I):	reaction coordinate		
resonance stiffening of internal rotation, $V_0 = 3 \rightarrow 13.0$ kcal/mol	−1.86	−1.72	−1.53
C–C, 1000 cm^{-1} → C$\dot{-}$C, 1200 cm^{-1}	−0.10	−0.20	−0.38
$\Delta S_3^{\circ\ddagger}$	−26.46	−26.61	−26.22

[a] Adjusted to give experimental A_3^H at $\langle T\rangle$ = 1000 K (log $(A_3^H/M^{-1}\,s^{-1})$ = 10.36).

k_3 at 500 K: log $(k_3/M^{-1}\,s^{-1}) = (9.67 \pm 0.30) - (3.20 \pm 1.50)/\theta$. $K_{4,3}$ at T = 500 K is then computed to be 7.54×10^{-7}, which yields a standard heat of formation ΔH°_f(benzyl) = 47.80 ± 1.50 kcal/mol at 300 K, using an estimate for S°(benzyl)[10] and C_p data[2,10] listed in Table VI.

The comparative rate shock-tube decomposition of isobutylbenzene at $\langle T\rangle$ = 1100 K yields ΔH°_f(benzyl) = 48.0 ± 2.0 kcal/mol[12] at 300 K under the assumption of zero activation energy (in pressure units) for the reverse reaction at reaction temperature (Arrhenius activation energy for decomposition $E_d = \Delta H^\circ$), a value markedly higher than the currently accepted value from iodination studies and related evidence[1] of 45.00 ± 1.5 kcal/mol. However, if one converts the measured Arrhenius activation energy for the decomposition of isobutylbenzene of 69.6 kcal/mol[12] into the thermodynamic function ΔH°_{300} by making the convenient assumption[6] that the activation energy for recombination at 0 K is zero,[15] one deduces ΔH°_f(benzyl) = 46.40 kcal/mol at 300 K. This method, however, necessitates the use of an appropriate model for the transition state. In this example, we used a rotational transition state[13] to deduce $\langle \Delta C_v^\ddagger\rangle$ in order to obtain the critical energy $E_{d,0}$ from the activation energy at 1100 K.

Thus, the total spread in $\Delta H^\circ_f(C_7H_7\cdot)$ amounts to 3 kcal; there are two points which are noteworthy when discussing this discrepancy. First, the accepted value of 45 ± 1 kcal/mol is based on an estimated rate for reaction 6 that is consistent with an activation energy of 1.0 ± 1 kcal/mol. In the present work, we have measured the rate and the activation energy for reaction 6, although for the deuterium system and at higher temperatures. Use of a reasonable transition-state model together with the measured isotope effect for the analogous allyl system leads to $\Delta H^\circ_f(C_7H_7\cdot)$ of 47.8 ± 1.5 kcal/mol. Secondly, as stated above, the "high" heat of formation of 48.0 kcal/mol from the single-pulse shock tube decomposition of isobutylbenzene[12] reduces to 46.40 kcal/mol if one makes a different assumption regarding the activation energy for the recombination reaction.

To summarize, it seems to us that the best value for $\Delta H^\circ_f(C_7H_7\cdot)$ is around 47.0 ± 1.0 kcal/mol on the basis of experimental evidence. A consistency check on $\Delta S^\circ_{4,3}$ and thus on the standard entropy of benzyl radical using the Arrhenius parameters A_3 and A_4 (2.30R log $A_4/A_3 = \Delta S^\circ_{4,3}$) could not be performed because of the lack of reliable Arrhenius parameters for the reverse of (7).[5] Instead, Arrhenius parameters were calculated for the reverse of (7), log A_4, E_4, using an estimate for $\Delta S^\circ_{4,3}$ (ref 2 and 10) at 500 K, the extrapolated rate constant k_3 (through transition-state model displayed in Table V), and the experimental rate for the reverse of (7) from the iodination study of toluene.[5] This method, that is described in some detail in part A dealing with allyl radical, yielded the rate parameters for k_4 at T = 300, 500, and 1000 K, listed in Table VI. The same observations can be made as in the allyl case when considering the magnitude of log A_4 and log A_3, respectively.

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Appendix

For a radical titration (metathesis) with HX, where X = I, Br, the pertinent reaction system is

$$R\cdot + HX \xrightarrow{k_a} RH + X\cdot \qquad (A\text{-}1)$$

$$R\cdot \xrightarrow{k_e^{R\cdot}} \qquad (A\text{-}2)$$

$$HX \xrightarrow{k_e^{HX}} \qquad (A\text{-}3)$$

Under steady-state conditions, the following expressions for the concentration of the involved species result

$$d(RH)/dt = k_a(R\cdot)(HX) - k_e^{RH}(RH) \equiv 0 \qquad (A\text{-}4)$$

$$d(R\cdot)/dt = R_R{}^i - k_e^{R\cdot}(R\cdot) - k_a(R\cdot)(HX) \equiv 0 \qquad (A\text{-}5)$$

$$d(HX)/dt = R^i{}_{HX} - k_e^{HX}(HX) - k_a(R\cdot)(HX) \equiv 0 \qquad (A\text{-}6)$$

where k_e^P is the escape rate constant of species P and $R_P{}^i$ is the

Table VI. Measured and Calculated Rate Parameters and Thermochemical Parameters for the Equilibrium[d] toluene + I· $\underset{k_3}{\overset{k_4}{\rightleftarrows}}$ benzyl + HI

T/K	log $(k_3/M^{-1}\,s^{-1})$	log $(k_4/M^{-1}\,s^{-1})$	$\Delta S^\circ_{4,3}$/eu[a]	$\Delta H^\circ_{4,3}$, kcal/mol	$\langle \Delta C_{p4,3}\rangle$[a]	$\langle \Delta C^\ddagger{}_{p3}\rangle$[c]
1000	log k_3^D *10.46 − 6.3/θ*	11.77 − 23.60/θ	6.46	17.30	0.43	0.56
1000	log k_3^H 10.36 − 5.5/θ					
500	9.67 − 3.20/θ	11.02 − 20.30/θ	6.16	17.08[b]	2.28	−0.30
300	9.26 − 2.50/θ	10.36 − 19.10/θ	5.0	16.62		

[a] Thermochemical estimate, ref 2 and 10. [b] From $K_{4,3} = k_4/k_3$ and $\delta S^\circ_{4,3}$. Values for $\delta H^\circ_{4,3}$ at 300 and 1000 K computed with $\langle \delta C_{p,4,3}\rangle$. [c] Calculated from $\delta S_3{}^{\circ\ddagger}$ of transition-state model in Table V. [d] Italicized values represent experimental results; others are calculated Arrhenius parameters (using transition-state model (10) from Table V, ($\theta = 2.303RT$ in kcal/mol).

flow rate of P into the VLPP reactor (in units of molecules s^{-1} L^{-1}). With the use of (A-4)–(A-6), (RH) can be expressed as a function of (HX):

$$(\mathrm{RH}) = \frac{k_a}{k_e^{\mathrm{RH}}}(\mathrm{R}\cdot)(\mathrm{HX}) = \frac{k_a}{k_e^{\mathrm{RH}}} \frac{R_{\mathrm{R}}^{\mathrm{i}\cdot}}{k_e^{\mathrm{R}\cdot} + k_a(\mathrm{HX})} \times \frac{R^{\mathrm{i}}_{\mathrm{HX}}}{k_e^{\mathrm{HX}} + k_a(\mathrm{R}\cdot)} \qquad \text{(A-7)}$$

(A-7) is simplified to give (A-8) under the condition (HX) ≫ (R·);

$$(\mathrm{RH})_\infty = \frac{k_a}{k_e^{\mathrm{RH}}} \frac{R_{\mathrm{R}}^{\mathrm{i}}}{k_a(\mathrm{HX})} \frac{R^{\mathrm{i}}_{\mathrm{HX}}}{k_e^{\mathrm{HX}}} \qquad \text{(A-8)}$$

With the definition $1/f = (\mathrm{RH})_\infty/(\mathrm{RH})$, the following expression is obtained, where $R^\circ_{\mathrm{HX}} = k_e^{\mathrm{HX}}(\mathrm{HX})$:

$$1/f = 1 + \frac{k_e^{\mathrm{R}\cdot} k_e^{\mathrm{HX}}}{k_a R^\circ_{\mathrm{HX}}} + \frac{R_{\mathrm{R}\cdot}^{\mathrm{i}}}{R^\circ_{\mathrm{HX}}} \qquad \text{(A-9)}$$

In the limit of high (HX), where $R^{\mathrm{i}}_{\mathrm{HX}} = R^\circ_{\mathrm{HX}}$ holds to a good approximation and where $R_{\mathrm{R}}^{\mathrm{i}}$ is negligible with respect to R°_{HX} and $R^{\mathrm{i}}_{\mathrm{HX}}$, respectively, (A-9) can be simplified to expression (A-10), which relates the experimental quantities $1/f$ and $R^{\mathrm{i}}_{\mathrm{HX}}$ to the desired rate constant k_a if the escape rate constants $k_e^{\mathrm{R}\cdot}$ and k_e^{HX} are known.

$$1/f = 1 + \frac{k_e^{\mathrm{R}\cdot} k_e^{\mathrm{HX}}}{k_a R^{\mathrm{i}}_{\mathrm{HX}}} \qquad \text{(A-10)}$$

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(14) The combined error limits have been estimated to be ±1.5 kcal/mol in view of the high-precision determinations of k_4 (ref 4).

(15) This assumption results in the following relations:[6] $E_{\mathrm{d,o}} = \Delta E^\circ{}_{\mathrm{o}}$; $\Delta E_{\mathrm{o}}{}^{T} = \Delta E^\circ{}_{\mathrm{o}} + T\langle \Delta C_v \rangle$, where $E_{\mathrm{d,o}}$ is the critical energy for the bond-breaking reaction.

Direct Measurement of Absolute Rates of Hydrogen Abstraction by *tert*-Butoxy Radicals. A Flash Photolysis Electron Spin Resonance Study

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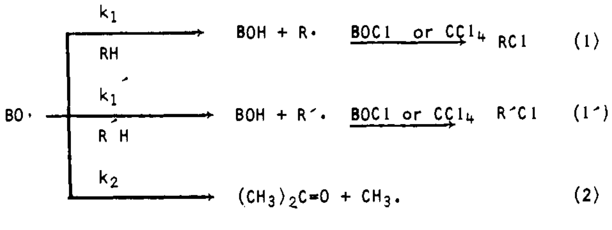
Abstract: The flash photolysis electron spin resonance spectroscopy is applied to direct monitoring of the growth of the product radicals from the hydrogen abstraction reaction to obtain the rate constant. Photolysis of di-*tert*-butyl peroxide is the source of *tert*-butoxy radicals. Cyclopentane, anisole, methyl *tert*-butyl ether, and methanol as hydrogen atom donors have been studied: the Arrhenius parameters log A (M^{-1} s^{-1}) and activation energy E_a (kcal/mol) per active hydrogen have been determined to be 9.1 and 6.1, 8.8 and 5.9, 8.8 and 5.2, and 8.6 and 5.3, respectively. The absolute rates (20 °C) are about a factor of 1.5 higher than the previous (indirect) estimates, but about a factor of 2 lower than a recent study by Scaiano et al. using optical laser flash photolysis.

This work was initiated for two major goals: (1) the production of radicals for CIDEP (chemically induced dynamic electron polarization) studies[1,2] by the photochemical decomposition of di-*tert*-butyl peroxide[3] (BOOB) and (2) the measurement of absolute rate constant of hydrogen abstraction reaction by *tert*-butoxy radicals (BO·). We failed to observe any CIDEP effect in the systems studied, but we were fortunate enough to be able to measure the absolute rate constants of some of the hydrogen abstraction reactions of BO·. Our method represents a more direct way than previously reported to measure these rate constants, which are still hard to come by.[4,5]

In 1960 Walling started reporting a series of a well-planned and elegant investigations on the rate of hydrogen abstraction reactions by *tert*-butoxy radicals.[6] A very large amount of relative rate constants have since been determined. The basic reaction used was the well-known radical chlorination of hydrocarbons by *tert*-butyl hypochlorite (BOCl). Relative reactivities of organic compounds toward BO· (k_1/k_1') may be measured in competitive experiments where two substances (RH and R′H) react with BO· and the product radicals then form products such as organic chlorides by reaction with hypochloride (or carbon tetrachloride if other initiators of BO· are used). See eq 1, 1′, and 2. The ratio of rate constants k_1/k_1' may be determined by estimating the relative yields of RCl and R′Cl or the consumption of reactants in competitive experi-



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