FREE-RADICAL AND MOLECULE THERMOCHEMISTRY FROM STUDIES OF GAS-PHASE IODINE-ATOM REACTIONS

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I. Introduction

The ultimate goal of the chemist is to be able to make accurate *a priori* predictions of the products and the rates of chemical reactions. At this stage in the development of chemistry, chemists are able to predict the products of a wide range of reactions and are beginning to have a more limited success in predicting rates.

Chemical reactions are, in general, made up of a number of "elementary" steps. Some combination of the rates of these steps determines the rate of the over-all process. It thus becomes necessary to know the rate constants or, better still, the activation parameters for those elementary steps. The activation parameters in turn are related to, and often accessible from, thermochemical parameters of reactants, products, and intermediates. The thermochemistry of short-lived intermediates is most accurately obtained from kinetic studies. This review is concerned with a specific class of such kinetic studies.

The vast majority of these particular reactions have been studied in these laboratories, and this review is undertaken in large measure, in the hope that others will discover the usefulness of the techniques discussed herein, and will add to the paucity of thermochemical data on free radicals.

We have tried to keep abreast of the literature through July 1968.

II. Background

A. MECHANISM

The gas-phase reactions of both aliphatic and aromatic iodides (RI) with HI go quantitatively to parent hydrocarbon (RH) and I_2 at measurable rates in the 200–500° temperature range.

$$RI + HI \rightleftarrows RH + I_2$$

In 1934, Ogg[1] measured the rates for the reactions with R equal to CH_3, C_2H_5, and n-C_3H_7. His interpretation of the results included a mechanism which was part radical chain and part bimolecular, and yielded rate constants which Benson and O'Neal[2a] and Sullivan,[2b] with the advantage of 25 years of increased understanding of the significance of Arrhenius parameters, showed to be inconsistent with parameters for similar reactions. These workers[2] have proposed the simple mechanism

$$\begin{aligned} I + M &\underset{r}{\overset{p}{\rightleftarrows}} 2I + M \quad K_{I_2} \\ RI + I &\underset{2}{\overset{1}{\rightleftarrows}} R + I_2 \\ R + HI &\underset{4}{\overset{3}{\rightleftarrows}} RH + I \end{aligned} \qquad \text{(i)}$$

and shown that Ogg's[1] data were consistent with this mechanism. Furthermore, it follows that if the entropy and heat of formation for the iodide (RI) are known, measurements of $\Delta H^\circ_{1,2}$ and $\Delta S^\circ_{1,2}$ may be used to obtain values of the heat of formation and entropy of the radical. Similarly, measurements of $\Delta H^\circ_{3,4}$ and $\Delta S^\circ_{3,4}$ yield the same information, if the values are known for the hydrocarbon. If one can measure, or

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(1) R. A. Ogg, Jr., *J. Amer. Chem. Soc.*, **56**, 526 (1934).

(2) (a) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **34**, 514(1 961); (b) J. H. Sullivan, *J. Phys. Chem.*, **65**, 722 (1961).

knows, the activation energies for either of the pairs, 1 and 2, or 3 and 4, one has measured the heat of formation of the radical. A reasonable amount of evidence has accumulated to indicate that $E_2 = 0 \pm 1$ and $E_3 = 1 \pm 1$ kcal/mole. (This represents a change, as prior to this time the value $E_3 = 1.5 \pm 1$ kcal/mole has been used.) Some of this will be discussed presently. In the meantime, accepting these as constant values means that measurements of E_1 or E_4 will yield the enthalpy of interest.

The above simple mechanism rests on the assumptions that I and I_2 are in equilibrium, and that the following reactions are negligible.

$$\mathrm{RI} \xrightarrow{a} \mathrm{R} + \mathrm{I}$$

$$\mathrm{R} + \mathrm{RI} \xrightarrow{b} \mathrm{RH} + \cdot\mathrm{R'I}$$

Steady-state analysis yields the relation

$$\frac{(\mathrm{R})}{(\mathrm{I})} = \frac{k_1(\mathrm{RI}) + k_4(\mathrm{RH})}{k_2(\mathrm{I_2}) + k_3(\mathrm{HI})} << 1$$

In consequence, the only important terminations are I-atom recombination. This is true even though I-atom recombination requires a third body,[3] whereas $\mathrm{R} + \mathrm{I} \rightarrow \mathrm{RI}$ or $2\mathrm{R} \rightarrow \mathrm{R_2}$ does not. Since initiation is I_2 decomposition, the first condition is achieved.

Reactions of type a could compete as initiation steps, if $DH°$(R–I) is very weak. This has not been observed.

Reactions of type b can never compete with reactions 2 and 3 and are totally unimportant since reactions 2 and 3 proceed at about 1 in 100 collisions, whereas reaction b probably has an *A* factor of 1 in 1000 and some considerable activation energy.

An interesting observation concerning the radical trapping ability of HI is that from the fact that the bond dissociation energy (BDE) is $DH°_{298}(\mathrm{H{-}I}) = 71.3$ kcal/mole, this is the strongest bond an I atom can make and one of the weakest that an H atom makes. This further implies that a radical R will always abstract H from HI, never I.

B. DISCUSSION OF ASSUMPTION THAT $E_2 = 0 \pm 1$ KCAL/MOLE

The values for $\Delta H_f°_{298}(\mathrm{R\cdot},g)$ obtained by the kinetic methods described in this review rest on the assumption that the activation energy for reaction 2 is 0 ± 1 kcal/mole. There are several experimental indications, if not proofs, of this statement.

Christie[4] has measured the rate constant k_2 at room temperature as part of an investigation of the oxidation of CH_3I. Her value, which is based on assigning a value of $10^{10.5}\ M^{-1}$ sec^{-1} to CH_3 radical combination, is $10^{10.0}\ M^{-1}$ sec^{-1}. Using Flowers and Benson's[5] value of $\log A_1 = 11.4\ M^{-1}$ sec^{-1}, and $\Delta S°_{12}(560\mathrm{K}°) = 6.2$ gibbs/mole, $\log A_2(560°\mathrm{K}) = 10.0\ M^{-1}$ sec^{-1}. Thus, $E_2 \approx 0$ kcal/mole.

Further evidence is the agreement between the I-atom method and photobromination work[6] on ethyl and *t*-butyl radicals. The photobromination values are obtained by measuring the activation energy E_x directly and the activation energy E_{-x} relative to E_2 for R = CH_3. All values are based on the assumption $E_2 \approx 0$. Thus, while the values of $DH°_{298}$ (CH_3–H) obtained by these two methods, which agree exactly, are based on the same assumption, the values for $DH°_{298}$ (C_2H_5–H) and $DH°_{298}$(t-C_4H_9–H), which also agree exactly, are based on $E_2 \approx 0$ for different R's. The agreement here bespeaks the fact that all E_2's are the same.

$$\mathrm{RH} + \mathrm{Br} \underset{-x}{\overset{x}{\rightleftharpoons}} \mathrm{R} + \mathrm{HBr}$$

Amphlett and Whittle,[7] using for the combination of CF_3 radicals $\log A_c = 10.36\ M^{-1}$ sec^{-1} and $E_c = 0.0 \pm 0.5$ kcal/mole, deduce that for R = CF_3, $\log A_2 = 9.42\ M^{-1}$ sec^{-1} and $E_2 = 0.0 \pm 0.5$ kcal/mole.

One of the best arguments for the assumption is that BDE's derived using it are generally transferable.[8]

Recently in the author's laboratory, a technique for measuring rate constants of reactions, such as 2 or 3, over wide temperature ranges (300–1000°) has been developed.[9a,b] Preliminary evidence is that k_3 (400°) for R = CH_3 is $\sim 10^9\ M^{-1}$ sec^{-1}, and very little change is seen at 1000°. This method has the great advantage of being independent of any other rate constant, such as combination. Rate constants are obtained relative only to effusion from a Knudsen cell. A program is underway to determine k_2 and/or k_3 for various R's.

The fact of the zero activation energy for reaction 2 raises the question of cause. There are many radical abstraction reactions which are exothermic, but all show activation energy. An explanation in this case may come from such evidence as the stability of the molecule I_3.[3] This stability must mean that I_2 can expand its valence shell and thus the species (RI_2) may also be stable and reaction 2 may be analogous to a radical–radical disproportionation reaction. Of course, the zero activation energy would then mean that the expansion of the valence shell would have to be a zero activation energy process itself.

It is also interesting to note that the activation energy in the exothermic direction, herein *defined* as the *intrinsic* activation energy (E_i) for reactions of the type $\mathrm{R} + \mathrm{HX} \rightarrow \mathrm{RH} + \mathrm{X}$ (X = F, Cl, Br, and I), is quite small, being 0, 1, 3, and 1 kcal/mole, respectively.[10]

C. UNCERTAINTIES

In this review, we have often taken the liberty of recalculating derived thermochemical quantities from measured rate parameters. This will often mean that the reader will find discrepancies between values quoted here and in earlier sources.

We have followed the general philosophy of treating the experimental data in what we *now* consider to be the correct way. Such treatment may lead to values of thermochemical parameters which are only slightly different from those originally reported. While we recognize that this could cause some confusion, it is our hope that this review will illustrate the uniform standards that should be applied to data of this type.

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(3) G. Porter, *Science*, **160**, 1299 (1968).

(4) M. Christie, *Proc. Roy. Soc.*, **A244**, 411 (1958).

(5) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, 38, 882 (1963).

(6) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).

(7) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **63**, 2695 (1967).

(8) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968.

(9) (a) S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc.*, 89, 2525 (1967); (b) S. W. Benson, D. M. Golden, and R. Jackson, Abstracts, S-191, 155th National Meeting of The American Chemical Society, San Francisco, Calif., March 1968.

(10) G. C. Fettis and J. H. Knox, *Progr. Reaction Kinetics*, **2**, 2 (1964).

We have indicated our preferred values in Table II, taking into account other measurements besides those reviewed here.

Error limits reported for a particular work are standard deviations, with a standard deviation of ±1 kcal/mole *assigned* to the values of E_2 and E_3 used.

The values of mean heat capacity $[\overline{\Delta C_p}^\circ = \frac{1}{2}(\Delta C_p{}^\circ{}_{298} + \Delta C_p{}^\circ{}_T)]$ used come from standard sources,[11] as well as from group additivity[8,12] and estimation methods for radicals discussed by Benson[8] and O'Neal and Benson.[13] An uncertainty of ±2 gibbs/mole was assigned to all values of $\overline{\Delta C_p}^\circ$, and $\Delta H^\circ{}_{298}$ reflects this error as well as those above. Additional errors in $\Delta H_f{}^\circ{}_{298}(\mathrm{R}\cdot,\mathrm{g})$ reflect the uncertainty in the heat of formation of the requisite RI and/or RH. Since $DH^\circ{}_{298}(\mathrm{R{-}H}) = \Delta H^\circ{}_{4,3}(298) - DH^\circ{}_{298}(\mathrm{H{-}I})$, the error in the BDE may be lower than the error in the heat of formation of the radical.

Our estimates of the best values are assigned a lower uncertainty than the individual measurements because of the precision of overlapping experiments.

III. Rate Expressions

The equilibrium constant for the over-all reaction A lies quite far to the right in the temperature range (500–800°K) suitable for kinetic studies for most R's. Thus, if one calculates the rate of I_2 formation using the steady-state approximation and neglecting k_4,[2] for reaction A eq 1 results.

$$\mathrm{RI + HI \rightleftarrows RH + I_2} \tag{A}$$

$$\frac{d(I_2)}{dt} = \frac{k_1 K_{I_2}{}^{1/2}(I_2)^{1/2}(\mathrm{RI})}{1 + k_2(I_2)/k_3(\mathrm{HI})}$$

$$= K_{1,2}K_{I_2}{}^{1/2}k_3\,\frac{(\mathrm{RI})(\mathrm{HI})}{(I_2)^{1/2}} \text{ for } k_2(I_2) \gg k_3(\mathrm{HI}) \tag{1}$$

$$= k_1 K_{I_2}{}^{1/2}(\mathrm{RI})(I_2)^{1/2} \text{ for } k_2(I_2) \ll k_3(\mathrm{HI})$$

Examination of this expression will show that the rate of appearance of I_2 with time should start off slowly and be catalyzed by I_2, which appears initially with a rate whose order in I_2 is one-half. After a time, the rate should then be inhibited by I_2, which has an order of negative one-half in the limit of large I_2/HI ratios. Such behavior has been observed in all cases studied, including the lack of HI dependence in the early stages of the reaction. The changing nature of this expression with I_2/HI ratios makes it convenient to break the data for such systems into two parts. The first part, when $0.01 < (I_2)/(\mathrm{HI}) < 0.1$, is treated according to eq 1 with an estimated value of k_2/k_3. (Note that since k_2/k_3 is of the order of 5 (see below), an error of ±10% in this value leads to errors in k_1 no greater than +3%.) The second part, when $0.1 < (I_2)/(\mathrm{HI}) < {\sim}2.0$, is best treated by rearranging (1) to

$$\frac{(I_2)}{(\mathrm{HI})} = \frac{k_1 k_3}{k_2}\left[\frac{K_{I_2}{}^{1/2}(\mathrm{RI})(I_2)^{1/2}}{d(I_2)/dt}\right] - \frac{k_3}{k_2} \tag{2}$$

and plotting $(I_2)/(\mathrm{HI})$ *vs.* the term in brackets. The slope divided by the intercept gives k_1 and the intercept k_3/k_2. (Note that values of k_3/k_2 obtained in this region can be used in the treatment of data by eq 1. Note as well, that practical upper limits of $(I_2)/(\mathrm{HI})$ are reached at the point where $d(I_2)/dt$ becomes so small that the error in measuring it is large.)

Determination of k_1 over a reasonable temperature range will then yield E_1. One also can use the temperature dependence of k_3/k_2 (*i.e.*, $E_3 - E_2$), as a consistency check on the assumption concerning these values.

There are several instances when this method develops difficulties. The first is when the $\Delta H_f{}^\circ$ of the iodide is not known, the second (discussed in section II) when the iodide is unstable with respect to homolytic scission of the C–I bond, thus complicating the kinetic expression by introducing a different initiation step, and, third, when the iodide is unstable with respect to HI elimination and olefin formation. These three difficulties can all be circumnavigated. (More difficult is the case when either of the decompositions is heterogeneous.)

The first above-mentioned difficulty can be eliminated by measuring the equilibrium constant of reaction A. Actually, since the equilibrium lies so far to the right in (A), practicality demands that one start with the hydrocarbon and I_2 and measure the equilibrium amounts of RI and HI. Usually entropies are either available or can be estimated with sufficient accuracy to justify a "third-law" measurement of the enthalpy. "Second-law" measurements are also possible.

If it is feasible to measure equilibrium in a homogeneous system (no catalyst), then the approach to equilibrium may also be followed, and one can measure k_4, and thus $\Delta H_f{}^\circ(\mathrm{R})$ with the same experiment. The rate expression is

$$\mathrm{RH + I_2 \rightleftarrows RI + HI} \tag{B}$$

$$\frac{d(\mathrm{RI})}{dt} = \frac{k_4 K_{I_2}{}^{1/2}(I_2)^{1/2}(\mathrm{RH})}{1 + k_3(\mathrm{HI})/k_2(I_2)}\left[1 - \frac{(\mathrm{RI})(\mathrm{HI})}{(\mathrm{RH})(I_2)}\frac{1}{K_{\mathrm{eq}}}\right] \tag{3}$$

which, since $(I_2) \gg (\mathrm{HI})$ and (RH) and (I_2) are essentially constant, becomes

$$\frac{d(\mathrm{RI})}{dt} = k_4 K_{I_2}{}^{1/2}(I_2)^{1/2}(\mathrm{RH})\left[1 - \frac{(\mathrm{RI})(\mathrm{HI})}{(\mathrm{RI})_{\mathrm{eq}}(\mathrm{HI})_{\mathrm{eq}}}\right] \tag{4}$$

Given the equilibrium and exothermicity of reaction 1, measurement of rates, starting from RI and HI, is accomplished at lower temperatures and with smaller quantities of reactants, thus minimizing the possibility of secondary reactions. On the other hand, secondary reactions are rare, owing to the radical trapping abilities of I_2 and HI, and starting from RH + I_2 leads to the rate constant k_4, unencumbered with the inhibition ratio k_3/k_2.

The difficulty of R–I bond breaking being a competing initiation step, which is serious only in cases where R is stabilized by delocalization, is overcome either by measuring the kinetics of RH + I_2, or starting the kinetic study of RI + HI with some I_2, as well.

The difficulty of HI elimination from the iodide adds complications, but can be handled by starting with RH + I_2 and taking into account the extra steps in the mechanism

$$\mathrm{RI} \underset{6}{\overset{5}{\rightleftarrows}} \text{olefin} + \mathrm{HI}$$

such that the over-all reaction produces olefin + 2HI. The kinetic expression is

$$\mathrm{RH + I_2 \rightleftarrows olefin + 2HI} \tag{C}$$

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(11) (a) F. D. Rossini, *et al.*, "API Tables," Carnegie Press, Pittsburgh, Pa., 1963; (b) D. R. Stull, Ed., "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1963.

(12) S. W. Benson, *et al.*, *Chem. Rev.*, in press.

(13) H. E. O'Neal and S. W. Benson, *Intern. J. Chem. Kinetics*, in press.

$$\frac{1}{2}\frac{\mathrm{d(HI)}}{\mathrm{d}t} = -\frac{\mathrm{d(I_2)}}{\mathrm{d}t} =$$

$$\frac{k_4 K_{\mathrm{I_2}}{}^{1/2}(\mathrm{I_2})^{1/2}(\mathrm{RH})\left[1 - \frac{(\text{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\frac{1}{K_{\mathrm{eq}}}\right]}{1 + k_3(\mathrm{HI})/k_2(\mathrm{I_2})\left[1 + \frac{k_1 K_{\mathrm{I_2}}{}^{1/2}(\mathrm{I_2})^{1/2}}{k_5}\right]} \tag{5}$$

This complicated expression simplifies extremely in those cases where the iodide is very unstable with respect to the olefin. Here the rate is controlled by step 4 of (i)

$$\frac{1}{2}\frac{\mathrm{d(HI)}}{\mathrm{d}t} = k_4 K_{\mathrm{I_2}}{}^{1/2}(\mathrm{I_2})^{1/2}(\mathrm{RH}) \tag{6}$$

If, however, the stability of iodide is such that K_{eq} is not very large, and k_5 is of moderate size, the expression becomes

$$Z = a_1 + a_2\frac{(\mathrm{HI})}{(\mathrm{I_2})^{1/2}} + b\frac{(\mathrm{HI})}{(\mathrm{I_2})} \tag{7}$$

where

$$Z = \frac{(\mathrm{RH})(\mathrm{I_2})^{1/2}\left[1 - \frac{(\text{olefin})(\mathrm{HI})^2}{(\mathrm{RH})(\mathrm{I_2})}\frac{1}{K_{\mathrm{eq}}}\right]}{\frac{1}{2}\frac{\mathrm{d(HI)}}{\mathrm{d}t}}$$

and $a_1^{-1} = k_4 K_{\mathrm{I_2}}{}^{1/2}$, $a_2^{-1} = k_6 K_{\mathrm{eq}}$, and $b = a_1(k_3/k_2)$. Often k_6 is known from independent experiments, and the a_2 term may be brought to the left-hand side of (7) so that a linear plot can be made.

There is another type of reaction, closely related to the above, that yields heats of formation of radicals. This is the iodine-catalyzed positional isomerization of olefins.

$$\text{olefin-1 }(\mathrm{O_1H}) + \mathrm{I_2} \underset{\mathrm{b}}{\overset{\mathrm{a}}{\rightleftarrows}} \text{olefin-2 }(\mathrm{O_2H}) + \mathrm{I_2} \tag{D}$$

$$\frac{-\mathrm{d(O_1H)}}{\mathrm{d}t} = (k_{\mathrm{a}} + k_{\mathrm{b}})K_{\mathrm{I_2}}{}^{1/2}(\mathrm{I_2})^{1/2}\left[(\mathrm{O_1H}) - \frac{(\mathrm{O_1H})_0}{1 + K_{\mathrm{a,b}}}\right] \tag{8}$$

where the mechanism is simply

$$\mathrm{O_1H} + \mathrm{I} \underset{3}{\overset{4}{\rightleftarrows}} \mathrm{O_{1-2}} + \mathrm{HI} \underset{3'}{\overset{4'}{\leftrightarrows}} \mathrm{O_2H} + \mathrm{I}$$

and neglecting the small (~1% at equilibrium) formation of the iodides

$$k_{\mathrm{a}} = \frac{k_4 k_3{}'}{k_3 + k_3{}'} \cong k_4/2$$

Thus, the heat of formation of the radical $\mathrm{O_{1-2}}$ can be ascertained by making use of the assumption concerning the activation energy of reaction 3.

IV. Experimental Methods

Gas-phase studies of the reactions described above lend themselves very nicely to spectroscopic investigation. Toward this end, Benson and coworkers[14] have employed a Cary 15 spectrophotometer which has been suitably modified so that the transmission of light may be measured through a quartz reaction vessel encased in an oven. Gas chromatographic analysis has also been employed.[15]

Reactions of the type A are followed most accurately by monitoring the appearance of $\mathrm{I_2}$ with time. This is done simply by following optical density at ~500 mμ, where only the $\mathrm{I_2}$ absorbs. Mass balance checks can be performed by measurements in the ultraviolet region where RI and HI and some of the RH's absorb.

The largest source of error is in the determination of $\mathrm{d(I_2)}/\mathrm{d}t$ (or $\mathrm{d(HI)}/\mathrm{d}t$). This quantity has usually been determined by drawing tangents to the $(\mathrm{I_2})$ *vs.* time curve over time increments (Δt), such that the $(\mathrm{I_2})$ increments $(\Delta \mathrm{I_2})$ were large compared to the error in determining them. Recently, time-sharing computer services have become available, and the slopes can be determined accurately by fitting the curve to a polynomial and taking the derivative.[16] In fact, the availability of the computer makes the integrated form of eq 1[5] usable, as well.

Reactions of the type B are followed by monitoring the appearance of absorbance in the ultraviolet, related to the formation of RI and HI. Mass balances at 500 mμ, while performed, are difficult since very little $\mathrm{I_2}$ is consumed. The same comments are appropriate here concerning the slope, as above.

In reactions of the type C, either $\mathrm{I_2}$ disappearance or HI appearance may be monitored, since the equilibrium is such that moderate-to-large amounts of $\mathrm{I_2}$ are consumed.

Gas chromatography can always be used to help check the mass balances, and, in the case of reactions of the type D, ratios of the olefins at various times determined by this method are the measured quantities desired when using the integrated form of eq 8.

All systems described herein have been shown to fit the simple mechanism, yet each system finds a way of turning up its own individual complexities, such that no measurement may be described as routine. The individual papers cited describe the specific trials and tribulations, not the least of which is heterogeneity of either the reactions in question (rare), or of side reactions (not uncommon).

These have always been overcome to some degree or other, and description of the methods is best left to the individual papers. A generally applicable solution to problems of heterogeneity has been the formation of a thin Teflon film in the reactor by putting some tetrafluoroethylene (gas phase) in the reactor, along with some initiator. One then scans the ultraviolet–visible range and removes the excess reactant before the windows become occluded.

V. Results

A. EQUILIBRIUM STUDIES

1. $RH + I_2 \rightleftarrows RI + HI$

The equilibrium constant for this type of reaction has been measured for various R's. These values determine the entropies and heats of formation of the various iodides.

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[14] D. M. Golden, R. Walsh, and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 4053 (1965).

[15] J. H. Knox and R. G. Musgrave, *Trans. Faraday Soc.*, **63**, 2201 (1967).

[16] S. Furuyama, D. M. Golden, and S. W. Benson, *Intern. J. Chem Kinetics*, in press.

Table I

Equilibrium Data

$RH + I_2 \rightleftharpoons RI + HI$	$\Delta H_f{}^{\circ}{}_{298}$ (RI,g), kcal/mole	$S^{\circ}{}_{298}$ (RI,g), gibbs/mole	Ref
R = CH_3	3.28 ± 0.16; 3.40 ± 0.05	60.47^a	14, 17
$C_6H_5CH_2$	30.43 ± 0.32	81.16 ± 0.71	*c*
C_3H_5	23.0 ± 0.6	77.8^a	*e*
CH_3CO	-30.3 ± 0.5	76.0^a	26
CF_3	-139.4 ± 0.17	73.32^a	36
$RI \rightleftharpoons olefin + HI$	$\Delta H_f{}^{\circ}{}_{298}(RI,g)$	$S^{\circ}{}_{298}(RI,g)$	*Ref*
olefin = isobutylene	-17.2 ± 0.3	82.5^l	20b
$RI_2 \rightleftharpoons olefin + I_2$	$\Delta H_f{}^{\circ}{}_{298}(RI_2,g)$	$S^{\circ}{}_{298}(RI_2,g)$	*Ref*
olefin = ethylene	-15.9 ± 0.2	83.3 ± 0.5	20a
propylene	8.6 ± 0.4	94.6 ± 1.0	20a
cyclopropane	10.6 ± 0.5^d	$93.0^{l,d}$	20a
acetylene	49.2 ± 0.1 (*trans*) 49.2 ± 0.1 (*cis*)	79.6^a (*trans*) 78.5 (*cis*)	*f*
$RH + I_2 \rightleftharpoons olefin + 2HI$	ΔH° (T, °K)	ΔS° (T, °K)	*Ref*
R = *i*-C_3H_7	-30.75 ± 0.4 (600)	-33.0 ± 0.5 (600)	*g*
t-C_4H_9	-27.1 ± 0.3 (550)	-37.8 ± 0.6 (550)	*h*
$olefin + I_2 \rightleftharpoons olefin + I_2$	$\Delta H^{\circ}{}_{298}$	$\Delta S^{\circ}{}_{298}$	*Ref*
Butene-1 ⇌ *trans*-butene-2	-2.8 ± 0.2	-3.1 ± 0.4	*i*
Pentene-1 ⇌ *trans*-pentene-2	-2.6 ± 0.1	-1.4 ± 0.1	*j*
Heptene-1 ⇌ *trans*-heptene-2	-2.7 ± 0.2	-1.2 ± 0.4	*k*
Heptene-1 ⇌ *trans*-heptene-3	-2.7 ± 0.2	-0.9 ± 0.4	*k*
cis- ⇌ *trans*-butene-2	-1.2 ± 0.2	-1.3 ± 0.2	*i*
cis- ⇌ *trans*-pentene-2	-0.75 ± 0.1	0.0 ± 0.4	*j*
cis- ⇌ *trans*-heptene-3	-0.90 ± 0.1	$+0.6 \pm 0.1$	*k*
cis- ⇌ *trans*-pentadiene-1,3^b	-1.00 ± 0.2	-0.1 ± 0.4	*l*
trans-heptene-2 ⇌ *trans*-heptene-3	0.05 ± 0.1	$+0.3 \pm 0.1$	*k*
cis- ⇌ *trans*-1,2-diiodoethylene	0 ± 0.1	$+1.1 \pm 0.1$	

[a] Third-law method using known or estimated S°(RI). [b] NO rather than I_2 catalyzed. [c] R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 650 (1966). [d] RI_2 is 1,3-diiodopropane. [e] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3194 (1966). [f] S. Furuyama, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **72**, 3204 (1968). [g] P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, 86, 2770 (1964). [h] H. Teranishi and S. W. Benson, *ibid.*, **85**, 2890 (1963). [i] D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964). [j] K. W. Egger and S. W. Benson, *ibid.*, **88**, 236 (1966). [k] K. W. Egger, *ibid.*, **89**, 504 (1967). [l] K. W. Egger and S. W. Benson, *ibid.*, **87**, 3311 (1965).

Often when measuring these equilibrium constants as a function of temperature, two methods of treating the data are available. The "second-law" method, involving the determination of the enthalpy and entropy changes for the reaction from the slope and intercept of a linear plot of log *K* *vs.* T^{-1} may be used, but precision is severely limited by the temperature range over which the study is made. If all the entropies are known, the "third-law" method may be used to evaluate the enthalpy change at any given temperature. In reactions of this type, the only entropy value that is likely to be unknown is that of RI, and often these values can be estimated to ±1 gibbs/mole.[8] The third-law method is inherently more precise, and, if a large temperature range is also feasible, any differences in thermochemical parameters between the two methods may often be a warning of systematic errors.

2. $RI_2 \rightleftharpoons olefin + I_2$

This reaction has been studied where the olefin is ethylene, propylene, and isobutylene, as well as acetylene. Cyclopropane is also conveniently placed in this grouping.

3. $RH + I_2 \rightleftharpoons olefin + 2HI$

Data are available for R = *i*-C_3H_7 and *t*-C_4H_9, affording in these particular cases confirmation of values for the enthalpy and entropy of hydrogenation, and demonstrating the usefulness of the I_2 technique for obtaining such values.

4. Positional and Geometric Isomerization of Olefins

The systems studied have been the positional isomerizations of butene-1 to butene-2, pentene-1 to pentene-2, heptene-1 to heptene-3, and heptene-2 to heptene-3, geometrical isomerizations of butene-2, pentene-2, pentadiene-1,3, heptene-2, heptene-3, and 1,2-diiodoethylene. These results lead to accurate values of the differences in enthalpy and entropy

Table II

Kinetic Data for Evaluating $\Delta H_f{}^{\circ}{}_{298}$ (R,g) and $DH^{\circ}{}_{298}$(R–H) from I-Atom Reactions[a]

R	*System*[b]	$\langle T\rangle$[c]	*Log* A_1[d]	E_1[e]	*Log* A_3/A_2	$E_3 - E_2$[e]
CH_3 (methyl)	A	560	11.4 ± 0.2	20.5 ± 0.5	−0.5 ± 0.4	0.8 ± 1.0
	B	583				
	A	550	10.7 ± ?	19.5 ± ?		
C_2H_5 (ethyl)	A	556	11.0 ± 0.3	17.1 ± 0.7	−0.6 ± 0.4	0.9 ± 1.0
	C	588				
n-C_3H_7 (*n*-propyl)	C	572				
i-C_3H_7 (isopropyl)	C	600				
	C	572				
sec-C_4H_9 (*sec*-butyl)	C	750				
t-C_4H_9 (*t*-butyl)	C	550			−0.1 ± 0.5	1.4 ± 0.7
	C	540				
HCO (formyl)	C	513			−1.0 ± 0.4	0.9 ± 0.9
CH_3CO (acetyl)	A	515	10.9 ± 0.2	14.6 ± 0.5	−0.5 ± 0.4	1.5 ± 1.0
	B	481				
$HOCH_2$ (hydroxymethyl)	C	589				
$(CH_3)_2(OH)C$ (2-hydroxyisopropyl)	C	527				
CH_3OCH_2 (methoxymethyl)	B	580			0.05 ± 0.2	0.9 ± 0.5
c-C_4H_7O (tetrahydrofuran-2-yl)	C	570			−0.1 ± 0.4	1.0 ± 1[l]
C_6H_5 (phenyl)	A	700	11.4 ± 0.1	28.4 ± 0.2	−0.5 ± 0.3	0.4 ± 1.0
C_2H_3 (vinyl)[i,k]	A	~640	11.2 ± ?	26.5 ± ?		
ICH_2 (iodomethyl)	A	522	11.5 ± 0.2	15.1 ± 0.4	−0.5 ± 0.5[k]	0.9 ± 1
I_2CH (diiodomethyl)	A	455	11.6 ± 0.1	9.4 ± 0.2	−0.5 ± 0.5[k]	0.9 ± 1
CF_3 (trifluoromethyl)	B	630				
	A	599	10.8 ± ?	17.6 ± ?		
	. .	554			−0.69 ± 0.03	0.51 ± 0.06
$CH_2\overline{\cdots}CH\overline{\cdots}CH_2$ (allyl)	B	527				
$CH_2\overline{\cdots}CH\overline{\cdots}CH(CH_3)$ (methylallyl)	D	519				
	C	750				
$CH_2\overline{\cdots}CH\overline{\cdots}CH\overline{\cdots}CH\overline{\cdots}CH_2$ (pentadienyl)	D	458				
$C_6H_5CH_2$ (benzyl)	B	513				
	A	?	?	4.1 ± ?		

[a] Values to the left of divider are experimental; values to the right are derived from them, based on key assumptions. [b] See text. [c] Mean temperature of measurement (°K). [d] M^{-1} sec^{-1}. [e] Kcal/mole. [f] Gibbs/mole; $\overline{\Delta C_p{}^{\circ}} = {}^1/_2[\Delta C_p{}^{\circ}{}_{T_m} + \Delta C_p{}^{\circ}{}_{298}]$; evaluated as discussed in ref 8. Uncertainty = ±2. [g] $\Delta H^{\circ}{}_{1,2}$ or $\Delta H^{\circ}{}_{4,3}$, depending upon whether E_1 or E_4 is measured. [h] Bond dissociation energy (BDE) derived from this particular I-atom experiment. [i] Selected from all available works, not just I-atom values. See S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965);

between isomers and may be combined with an independent value to obtain heats and entropies for a whole set of isomers.

The results and references are found in Table I.

B. KINETIC STUDIES

1. *Free-Radical Heat of Formation*

Employing the various rate expressions discussed above, many simple free radicals have been investigated. The apparent universal applicability of the simple mechanism gives confidence in the generality of these methods for determining radical thermochemistry.

a. $CH_3\cdot$ (Methyl)

Flowers and Benson[5] (FB) spectrophotometrically followed the appearance of I_2, using system A [$RI + HI \rightleftarrows RH + I_2$] and rate expression 2. The rate parameters they obtained are listed in Table II.

The value of $\Delta H^{\circ}{}_{1,2}$(298°K) determined by FB is sufficient to yield a value of the bond dissociation energy (BDE) $DH^{\circ}{}_{298}(CH_3\text{–}I)$, but, in order to obtain the heat of formation of CH_3, a value of $\Delta H_f{}^{\circ}{}_{298}(CH_3I, g)$ is needed.

Golden, Walsh, and Benson[14] measured the equilibrium constant for system B and combined their results (shown in Table I) with those of FB to obtain $\Delta H_f{}^{\circ}{}_{298}(CH_3,g)$ = 34.1 ± 1.2 kcal/mole.

Goy and Pritchard[17] also measured the equilibrium constant for system B, as well as the rate constant k_4. From their value of E_4 = 35.0 ± 1.1 kcal/mole, and E_3 = 1 ± 1 kcal/mole, $\Delta H^{\circ}{}_{298}(CH_3,g)$ = 34.8 ± 1.6 kcal/mole may be derived.

Boyd, *et al.*,[18] report values of A_1 and E_1, which are slightly different from those of FB, but give very little information concerning the experimental parameters.

b. $C_2H_5\cdot$ (Ethyl)

Hartley and Benson[19] followed the appearance of I_2, using

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(17) C. A. Goy and H. O. Pritchard, *J. Phys. Chem.*, **69**, 3040 (1965).
(18) R. K. Boyd, *et al.*, *ibid.*, **67**, 719 (1963).
(19) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

Log A_4[d]	E_4[e]	ΔC_p°[f]	$\Delta H^\circ(298^\circ K)$[e,g]	$\Delta H_f{}^\circ{}_{298}(R,g)$[e]	$DH^\circ_{298}(R\text{–}H)_I$[e,h]	$DH^\circ_{298}(R\text{–}H)$[e,i]	Ref
		1.22	20.2 ± 1.2	34.1 ± 1.2	104.1 ± 1.2		5, 14
12.0 ± 0.4	35.0 ± 1.1	1.8	33.5 ± 1.6	34.8 ± 1.6	104.8 ± 1.6	104 ± 1	17
		1.2	18.9 ± ?	32.8 ± ?	102.8 ± ?		18
		−1.0	17.4 ± 1.3	25.9 ± 1.3	98.2 ± 1.3	98 ± 1	19
11.1 ± 0.6	26.4 ± 1.5	−0.3	25.3 ± 1.9	24.3 ± 1.9	96.6 ± 1.9		15
11.9 ± 0.5	29.6 ± 1.4	1.1	28.3 ± 1.8	22.6 ± 1.8	99.3 ± 1.8	98 ± 1	15
11.2 ± 0.4	25.0 ± 1.0	0.6	23.8 ± 1.5	18.2 ± 1.5	95.1 ± 1.5	95 ± 1	21
11.0 ± 0.7	23.8 ± 1.9	0.4	22.7 ± 2.2	17.1 ± 2.2	94.0 ± 2.2		15
11.4 ± ?	25.6 ± ?	0.5	24.0 ± ?	13.0 ± ?	95.3 ± ?	95 ± 1	22
10.9 ± 0.2	21.4 ± 0.5	−2.3	21.0 ± 1.2	7.6 ± 1.2	91.8 ± 1.2	92 ± 1	23
11.3 ± 0.4	22.6 ± 1.1	−2.3	22.2 ± 1.6	8.8 ± 1.6	93.0 ± 1.6		15
10.9 ± 0.1	17.4 ± 0.1	1.3	16.2 ± 1.0	7.7 ± 1.9	87.5 ± 1.0	87 ± 1	24
		−2.3	15.1 ± 1.3	−4.7 ± 1.3	87.1 ± 1.3	87 ± 1	25, 26
10.3 ± 0.3[k]	15.7 ± 0.7	0.0	14.7 ± 1.3	−5.7 ± 1.3	86.1 ± 1.3		26
11.5 ± 0.4	26.0 ± 0.9	1.3	24.6 ± 1.5	−4.2 ± 1.5	95.9 ± 1.5	94 ± 2	27
11.1 ± 0.1	20.5 ± 0.2	−0.5	19.6 ± 1.1	−26.6 ± 1.1	90.7 ± 1.1	91 ± 1	29
11.5 ± 0.2	23.2 ± 0.4	1.2	21.9 ± 1.2	−6.9 ± 1.2	93.2 ± 1.2	93 ± 1	30
11.7 ± 0.2	21.5 ± 0.6	0[m]	20.5 ± 1.5	−4.3 ± 1.5	91.8 ± 1.5	92 ± 1	31
		−3.0	28.9 ± 1.3	80.0 ± 1.3	112.3 ± 1.3	112 ± 1	32
			26.5	≥68	≥108	≥108 ± 2	33
		−0.4	15.2 ± 1.2	55.0 ± 1.6	103.8 ± 1.6	103 ± 2	34
		0.2	9.4 ± 1.2	79.8 ± 2.2	102.7 ± 2.5	103 ± 2	35
10.6 ± 1.0	36.3 ± 3	1.1	34.9 ± 3.2	112.0 ± 3.6	106.2 ± 3.2	106 ± 1	36
		−1.3	18.0 ± ?	110.8 ± ?	107.4 ± ?		18
							7
10.2 ± 0.1	18.0 ± 0.3	−1.2	17.3 ± 1.1	41.4 ± 1.1	88.6 ± 1.1	89 ± 1	38
9.3 ± 0.3	12.4 ± 0.6	1.2	11.2 ± 1.3	30.4 ± 1.3	82.5 ± 1.3	83 ± 1	39
10.0 ± ?	15.3 ± ?	1.0	13.8 ± ?	33.0 ± ?	85.1 ± ?		22
9.5 ± 0.2	9.6 ± 0.3	0.6	8.5 ± 1.0	52.9 ± 1.0	79.8 ± 1.0	80 ± 1	40
8.4 ± 1.2	14.4 ± 2.2	2.0	13.0 ± 3.1	44.2 ± 3.1	84.3 ± 3.1	85 ± 1	41
		?	∼4.1 ± ?	45.1 ± ?	85.2 ± ?		18

J. A. Kerr, *Chem. Rev.*, 66, 465 (1966); and S. W. Benson; "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968

[j] Complicated by HI addition to vinyl iodide. [k] This was a one-temperature study. The *A* factor is an estimate. [l] Assigned as 1 kcal/mole

[m] No data available; error taken as ±3 gibbs/mole.

system A and rate expression 2. These, combined with the known value for $\Delta H_f{}^\circ{}_{298}(C_2H_5I,g) = -2.13$ kcal/mole,[20] lead to $\Delta H_f{}^\circ{}_{298}(C_2H_5,g) = 25.9 \pm 1.3$ kcal/mole.

Knox and Musgrave (KM),[15] using gas chromatographic techniques and system C, measured k_4, and their E_4 leads to $\Delta H_f{}^\circ{}_{298}(C_2H_5,g) = 24.3 \pm 1.9$ kcal/mole. They prefer to modify their Arrhenius parameters, such that $E_4 = 27.6$, and thus $\Delta H_f{}^\circ{}_{298}(C_2H_5,g) = 25.5 \pm$? kcal/mole.

c. n-$C_3H_7\cdot$ (n-Propyl)

Knox and Musgrave[15] have also measured k_4 for n-propyl, using system C, from which may be obtained a value $\Delta H_f{}^\circ{}_{298}$ (n-C_3H_7,g) = 22.6 ± 1.8 kcal/mole. This would lead to a primary C–H BDE of 99.3 ± 1.8 kcal/mole. The authors preferred value of $E_4 = 28.9$ would yield $DH^\circ_{298}(n\text{-}C_3H_7\text{–}H) = 98.6$ kcal/mole.

d. i-$C_3H_7\cdot$ (i-Propyl)

Nangia and Benson[21] used system C and eq 7 to obtain k_4. Their value of E_4 yields $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7,g) = 18.2 \pm 1.5$ kcal/mole.

KM[15] have measured the same rate constant in the same system and have obtained a value which leads to $\Delta H_f{}^\circ{}_{298}$($i$-$C_3H_7$,g) = 17.1 ± 2.2 kcal/mole. The authors list a preferred value of E_4 that is greater by 0.9 kcal/mole. This preferred value is arrived at, presumably by adjusting the preexponential factor to be one-half that for primary H abstraction in propane.

e. *sec*-$C_4H_9\cdot$ (*sec*-Butyl)

Chekkov, Tsailingol's, and Ioffe[22] have used system C with a high-temperature flow experiment to measure k_4. Inter-

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(20) (a) S. W. Benson and A. Amano, *J. Chem. Phys.*, 36, 3464 (1962); (b) *ibid.*, 37, 197 (1962).

(21) P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, 86, 2773 (1964).

(22) E. E. Chekhov, A. L., Tsailingol's, and I. I. Ioffe, *Neftekhimiya*, 7, 717 (1967); *Chem Abstr.*, 68, 48759*k* (1968).

preting the rate constants given in *Chemical Abstracts* to be $k_4K_{I_2}^{1/2}$ with units of $M^{-1/2}$ sec^{-1}, one obtains log k_4 = 11.4 ± ? −(24.6 ± ?)/θ M^{-1} sec^{-1} at T_m = 750°K.

The value of A_4 compares well with all others, and E_4 = 25.6 ± ? leads to $DH°_{298}$(*sec*-butyl–H) = 95.3 ± ?, in excellent agreement with $DH°_{298}$ (isopropyl–H).

f. *t*-C_4H_9· (*t*-Butyl)

Teranishi and Benson (TB)[23] have used system C and eq 7 to obtain k_4. They report E_4(500°K) = 21.4 ± 0.5, which leads to $\Delta H_f°_{298}$(*t*-C_4H_9,g) = 7.6 ± 1.2 kcal/mole. $DH°_{298}$(*t*-C_4H_9–H) = 91.8 ± 1.2 kcal/mole.

KM[15] again using the same system have obtained E_4 (540°K) = 22.6 ± 1.1 kcal/mole, and thus values 1.2 kcal/mole greater than TB. KM, however, prefer a value of 0.7 kcal lower than their measured number.

g. HCO· (Formyl)

Walsh and Benson[24] have used system C in a case where eq 6 may be used for initial values to determine k_4. They then also determined k_3/k_2 by adding HI. They obtain a value consistent with an 87.5 ± 1.1 kcal/mole value for $DH°$(H–CHO). [$\Delta H_f°_{298}$(CHO·,g) has a higher error, since $\Delta H_f°_{298}$ for formaldehyde is not well known.]

h. CH_3CO· (Acetyl)

O'Neal and Benson,[25] as amended by Walsh and Benson,[26] using system A obtained a value of E_1(515°K) = 14.6 ± 0.5, which yields $\Delta H_f°_{298}$(CH_3CO,g) = 4.7 ± 1.3 kcal/mole.

Walsh and Benson[26] have used system B at one temperature to determine k_4 and have used a value of $10^{10.3}$ for A_4.[25] This leads to a value of $\Delta H_f°_{298}$(CH_3CO,g) = 5.7 ± 1.3 kcal/mole, and this suggests that −5.2 would be a good value. The error limits may then be ±1 kcal/mole. This leads to $DH°_{298}$(CH_3CHO) = 87 ± 1 kcal/mole.

i. ·CH_2OH· (Hydroxymethyl)

Cruickshank and Benson[27] have measured the rate of the reaction of I_2 with CH_3OH, a system like C, except that the formaldehyde thus formed would itself react to give CO and HI. From a study, made difficult by surface effects, they concluded that the C–H BDE is greater than 95.9 ± 1.5 kcal/mole. This value combined with the value of ≤92 kcal/mole from photobromination studies[28] makes 94 ± 2 kcal/mole seem reasonable.

j. $(CH_3)_2\dot{C}(OH)$· (2-Hydroxypropan-2-yl)

Walsh and Benson[29] showed that the effect on the BDE of a tertiary C–H bond of substituting OH for CH_3 was very small. Using system C, they found $\Delta H_f°_{298}$[$(CH_3)_2\dot{C}(OH)$,g] = −27.1 ± 1.1 kcal/mole and $DH°_{298}$[$(CH_3)_2C(OH)$–H] = 90.2 ± 1.1 kcal/mole.

k. CH_3OCH_2· (Methoxymethyl)

Cruickshank and Benson[30] have studied the rate of abstraction of H by I from dimethyl ether, using system B. The iodide is stable here, as there is no elimination of HI possible. Their results indicate that there is no substantial difference between the C–H bond here and that in CH_3OH. They have also been able to ascertain the equilibrium constant at various temperatures and from a "second-law" treatment have shown that the entropy of CH_3OCH_2I is quite a bit lower than that of $CH_3CH_2CH_2I$, indicating perhaps a strong dipolar interaction hindering internal rotation.

l. *c*-C_4H_7O· (Tetrahydrofuran-2-yl)

Cruickshank and Benson[31] have studied this system. The products are furan and HI, so that system C equations are applicable. Once again, as with other oxygen-containing compounds, there are surface problems, but they manage to overcome these and to show that the BDE for the α-H's is 92 ± 2 kcal/mole.

m. C_6H_5· (Phenyl)

Rodgers, Golden, and Benson,[32] using system A, have shown that $DH°_{298}$(C_6H_5–H) = 112.3 ± 1.5 kcal/mole. This value is 5–10 kcal higher than previously believed and has had a great effect on the choice of mechanisms for most aromatic substitution reactions. In particular, it appears unlikely that H-atom abstractions from the aromatic ring ever takes place.

This is the highest BDE ever measured by this method.

n. C_2H_3· (Vinyl)

Rodgers, Golden, and Benson[33] have used system A with vinyl iodide and HI. Unfortunately, this system is complicated by the addition of HI to the vinyl group, and the only information abstractable from the data is $DH°_{298}$(C_2H_3–H) ≥ 108 ± 2 kcal/mole, and therefore the π-bond energy in C_2H_4 is equal to or greater than 70 kcal/mole.

o. ·CH_2I (Iodomethyl)

Furuyama, Golden, and Benson[34,35] have used system A, where R = CH_2I and thus RI = CH_2I_2 and RH = CH_3I, to obtain E_1 = 14.1 ± 0.4, and thus $DH°_{298}$(H–CH_2I) = 103.8 ± 1.6 kcal/mole, a number which is surprisingly similar to $DH°_{298}$(H–CH_3).

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(23) H. Teranishi and S. W. Benson, *J. Amer. Chem. Soc.*, 85, 2887 (1963).

(24) R. Walsh and S. W. Benson, *ibid.*, 88, 4570 (1966).

(25) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 37, 540 (1962).

(26) R. Walsh and S. W. Benson, *J. Phys. Chem.*, 70, 3751 (1966).

(27) F. Cruickshank and S. W. Benson, *ibid.*, in press.

(28) E. Buckley and E. Whittle, *Trans. Faraday Soc.*, 58, 536 (1962).

(29) R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, 88, 3480 (1966).

(30) F. Cruickshank and S. W. Benson, *Int. J. Chem. Kinetics*, in press.

(31) F. Cruickshank and S. W. Benson, *J. Amer. Chem. Soc.*, in press.

(32) A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, 89, 4578 (1967).

(33) A. S. Rodgers, D. M. Golden, and S. W. Benson, unpublished work.

(34) S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinetics*, in press.

(35) S. Furuyama, D. M. Golden, and S. W. Benson, *ibid.*, in press.

p. $\cdot CHI_2$ (Diiodomethyl)

Furuyama, Golden, and Benson[35] have again used system A where now R = CHI_2 to obtain $E_1 = 9.4 \pm 0.2$, and thus $DH°_{298}(CHI_2\text{–}H) = 102.7 \pm 2.5$ kcal/mole, showing that the addition of I atoms does not weaken the C–H bond very much, if at all. The large uncertainty in BDE is due to the uncertainty in $\Delta H_f°_{298}(CHI_3,g)$, which is extrapolated to 59.8 kcal/mole.

q. $CF_3\cdot$ (Trifluoromethyl)

Goy, Lord, and Pritchard[36] have used system B and obtained $E_4 = 36.3 \pm 3$. The value obtained for $DH°_{298}(CF_3\text{–}H)$ is 106.2 ± 3.2 kcal/mole, which despite the large error agrees well with other values[37] from the bromination and chlorination of fluoroform, as well as that from the use of system A by Boyd, *et al.*[18]

Amphlett and Whittle[7] have determined k_3/k_2 independently for R = CF_3.

r. $CH_2{=}CHCH_2\cdot$ (Allyl)

Golden, Rodgers, and Benson,[38] using system B, have obtained $E_4 = 18.0 \pm 0.3$ kcal/mole. This leads to $\Delta H_f°_{298}(C_3H_5,g) = 41.4 \pm 1.1$ kcal/mole and $DH°_{298}(C_3H_5\text{–}H) = 88.6 \pm 1.1$ kcal/mole. Comparing this to $DH°_{298}(n\text{-}C_3H_7\text{–}H) = 98 \pm 1$, the stabilization energy in allyl radical is 10 ± 1.5 kcal/mole.

s. $CH_2{=}CHCHCH_3\cdot$ (Methylallyl)

Egger, Golden, and Benson,[39a] as well as Benson, Bose, and Nangia[39b] have used system D (the positional isomerization of butene) to determine k_4. Their value of $E_4(519\,°K) = 12.4 \pm 0.6$ kcal/mole leads to $\Delta H_f°_{298}(C_4H_7,g) = 30.4 \pm 1.3$ kcal/mole and $DH°_{298}(C_4H_7\text{–}H) = 82.5 \pm 1.3$. Comparing this to $DH°_{298}(sec\text{-}C_4H_9\text{–}H) = 95 \pm 1$ kcal/mole, the stabilization energy in the methyallyl radical is 12.5 ± 1.5 kcal/mole.

Chekhov, Tsailingol's, and Ioffe[22] have also obtained k_4 using system C. Their value, as best ascertained from *Chemical Abstracts*, is $\log k_4(750\,°K) = 10.0 - (15.3/\theta)\ M^{-1}\ sec^{-1}$, which leads to $\Delta H_f°_{298}(C_4H_7,g) = 33.0$, and stabilization of ~10 kcal/mole. It is difficult to judge what weight should be given this work, as no error limits are available. Most examples of methallylic stabilization seem to be *ca.* 12 or 13 kcal/mole, but 3-kcal differences may be undetectable because of uncertainties in other quantities. Their value for A_4 also seems high, comparing with the value for R = allyl. On the other hand, their values for *sec*-butyl radical obtained in the same system are reasonable.

t. $CH_2{=}CHCHCH{=}CH_2\cdot$ (Pentadienyl)

Egger and Benson[40] have used system D once again to measure $E_4(458\,°K) = 9.60 \pm 0.25$ kcal/mole. Thus $\Delta H°_{4,3}(298\,°K) = 8.5 \pm 1$ kcal/mole and $DH°_{298}(\text{pentadienyl–H}) = 79.8 \pm 1$ kcal/mole, which represents a stabilization of 15 ± 1.5 kcal/mole, when compared to $DH°_{298}(sec\text{-C–H}) = 95.0 \pm 1$ kcal/mole.

u. $C_6H_5CH_2\cdot$ (Benzyl)

Walsh, Golden, and Benson,[41] in a study in which they determined accurate thermochemical parameters for benzyl iodide, also cursorily followed the rate in system B. They found that $DH°_{298}(\text{benzyl–H}) = 84.3 \pm 3.1$ kcal/mole, which adequately fixed the value at 85.0 ± 1 kcal/mole from other available values.[42] This means that the stabilization energy in the benzyl radical is 13 ± 1.5 kcal/mole.

2. *Pyrolysis of Organic Iodides*

It has been shown that the pyrolyses of organic iodides take place through simple eliminations and through the atom and radical processes discussed above.

The pyrolysis of alkyl iodides is controlled largely by the dehydroiodination of the iodide. (In the case of diiodides, deiodination occurs.) These reactions seem to occur by two pathways: one a unimolecular elimination, the other an I-atom-catalyzed path. Kinetic parameters have been reported, and it has been suggested[16] that the catalyzed pathway includes some contribution from donor–accepter complexes.

Benson and co-workers[16,43] have argued that the pyrolysis of 1,2-diiodoethylene and 1,2-diiodoethane, as well as *n*-propyl iodide, *n*-butyl iodide, *sec*-butyl iodide, isobutyl iodide, and ethyl chloride (in the presence of I atoms), all show a concerted I-atom-catalyzed step in which the olefin is formed, together with I_2, HI, or HCl, as the case may be. Where quantitative measures of the rate constants of these reactions are available, they all have activation energies only slightly in excess of the endothermicity ($\Delta E°$). Since I-atom addition to olefins is ~6 kcal/mole endothermic, a radical mechanism is ruled out for these systems. The HI eliminations have A factors of the order of $10^{10}\ M^{-1}\ sec^{-1}$, while the I_2 elimination A factor is about $10^{11.5}\ M^{-1}\ sec^{-1}$. In the pyrolyses, these are followed by the rapid RI + HI atom and radical reactions.

VI. Discussion

There is every indication that the values of $DH°(R\text{–}H)$ for ethyl, isopropyl, and *t*-butyl radicals are characteristic of primary, secondary, and tertiary C–H bonds.[44a,b] This statement which is equivalent to a statement that the rule of bond additivity applies[12] to $\Delta H_f°$ of the radical allows the calculation of the heat of formation of any unstabilized radical, since the heats of formation of RH are usually known or easily estimated.

The values for the BDE's $DH°(H\text{–}CH_2OH)$, $DH°[H\text{–}CH(CH_3)OH]$, and $DH°[H\text{–}C(CH_3)_2OH]$ are interesting. The first is 94 and the third is 91 kcal/mole. The second is

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probably ~92, as the same sort of photobromination experiments which give ≤92 for methanol and ≤90 for ethanol.[45]

The differences in the C–H BDE's are reflected in the π-bond strength defined as the difference between the O–H BDE in the alcohol and the O–H BDE in the radical formed from removing the H atom discussed above. Such a definition leads to π-bond strengths in acetone, acetaldehyde, and formaldehyde of 78, 76, and 73 kcal/mole, respectively. The transferability of the π bond in olefins is well known, the similarly defined quantities of isobutylene, propylene, and ethylene being 58, 59, and 59 kcal/mole, respectively. A comparison of these two sets would seem to indicate an opposite effect of CH_3 groups on the two types of π bonds. These differences warrant the attention of those who wish to quantitatively describe chemical bonding.

Values of the strength of the dative bond in C≡O, defined similarly to that of the π bond, can be obtained from both the formyl and acetyl radical values of Table II. Both give values of ~68 kcal/mole, as do other available data on compounds of the type CH_3COX and XCOX.

The stabilization energies discussed previously are defined operationally as the difference between the appropriate alkyl C–H bond and the C–H bond to the radical in question. The magnitude of these energies had been a question of some debate until recently, but the values presented here seem to be agreed on at present.

The more recently measured value of the stabilization energy in the allyl radical (10 kcal/mole) probably means that the value in the methylallyl radical (12.5 kcal/mole) includes a stabilization effect due to the extra methyl group which one might call an inductive effect. Note, however, that the stabilization energy in pentadienyl radical (15 kcal/mole) indicates that the extra vinyl group has an effect only half as great as the first. An attempt at explaining this has been based on the concept that the stabilization in allyl radical is due to simple delocalization of the extra electron in the manner depicted by the valence-bond structures[40]

The methyl inductive effect is due to the stabilization of the partial positive charge by a methyl group. The pentadienyl radical is written

and, if the stabilization energy in allyl radical is due in part to lessening of electron–electron repulsion, and in part due to the electrostatic interaction of the positive and negative ends, one might expect pentadienyl to have roughly twice the former, but less of the latter.

The high value of the C–H bond dissociation energy in benzene is a departure from earlier values and has implications for the mechanism of aromatic substitution and addition. Radicals almost surely add to aromatic rings, to form the cyclohexadienyl type of radical, which itself has ~25 kcal/mole of stabilization energy, rather than abstract the strongly bound H atom. This would appear to be true of the vinyl C–H BDE as well.[31]

In summary, BDE's measured by the techniques described here are among the most accurately determined and are the type of measurements needed, both to formulate a quantitative theory of chemical bonding and to have a thermochemical base on which to found the *a priori* estimation of activation parameters. At the same time, it should be kept firmly in mind that in calculating a rate constant, cumulative errors might exceed 2 kcal/mole, a number which in itself represents a factor of about 10 in rate of convenient temperatures.

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