

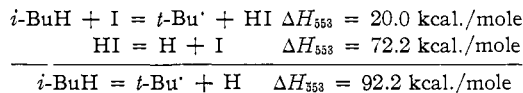
ΔS_B the entropy change of eq. B calculated from the thermodynamic data, $\log (A_2/A_3)$ is also given as

$$\log (A_2/A_3) = 10.88 - 10.7 - 0.26 = -0.08 \approx 0 \quad (8)$$

and $A_2/A_3 \approx 1$ is quite reasonable.

As shown in Table I, the values of inhibition constant k_2/k_3 changes from 0.226 to 0.251 depending on the temperature change of about 60°K., that is about 11% increase, and the average k_2/k_3 value is 0.24. The latter value gives, assuming $A_2/A_3 = 1$, 1.6 kcal./mole for $E_2 - E_3$, and this result shows good coincidence with the results of eq. 7. From $E_2 - E_3 = 1.6$ we find $(k_2/k_3)_{583^\circ} / (k_2/k_3)_{523^\circ} \approx 1.16$, that is, 16% increase with the temperature change of 60°K., and this result also shows good coincidence with those of experimental results.

Assuming $E_3 \approx 0$, E_2 may be considered as 1.4 kcal./mole at 523 ~ 583°K. Thus the heat of formation of the step 1 is given as 20.0 ± 0.7 kcal./mole. The bond dissociation energy of tertiary C-H bond, that is, the enthalpy change for the reaction $i\text{-BuH} \rightarrow t\text{-Bu}\cdot + \text{H}$, can be given as follows.



If we assume that the heat capacities of isobutane and the t -butyl radical are approximately equal, then the bond dissociation energy at 25°, $D^\circ(t\text{-Bu-H})$, is calculated as 90.9 ± 0.7 kcal./mole, which shows good coincidence with 91.1 ± 0.5 kcal./mole given by Eckstein, Scheraga, and Van Artsdalen from their bromination experiments.⁹

From the value of 90.9 kcal./mole for the bond dissociation energy, the heat of formation of the t -butyl radical is given as

$$\begin{aligned} \Delta H_f^\circ(t\text{-Bu}\cdot) &= \Delta H_f^\circ(i\text{-BuH}) - \Delta H_f^\circ(\text{H}) + D^\circ(t\text{-Bu-H}) \\ &= -32.1 - 52.1 + 90.9 = 6.7 \text{ kcal./mole} \end{aligned}$$

Hence the heat of formation of the t -butyl radical at 25° and 1 atm. is 6.7 ± 0.7 kcal./mole.

(9) This agreement unfortunately can only be looked upon as an extraordinary coincidence since the corresponding value of $E_2 - E_3 = 8$ kcal. found for the bromine system is quite unreasonable and unbelievable. It requires $A_2/A_3 \approx 10^6$ which is equally unbelievable.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Thermodynamics of the Homogeneous, Gas Phase Dehydrogenation of Isobutane^{1a}

By HIROSHI TERANISHI^{1b} AND SIDNEY W. BENSON

RECEIVED APRIL 8, 1963

The gas-phase equilibrium of the reaction $i\text{-C}_4\text{H}_{10} + \text{I}_2 \rightleftharpoons i\text{-C}_4\text{H}_8 + 2\text{HI}$ has been studied in the temperature range 522.5 to 582.9°K., analyzing for I_2 and HI *in situ*, spectrophotometrically. The experimental data yield for the equilibrium constant, $\log K_p(\text{atm.}) = -(25900 \pm 300)/4.575T + 8.130$. The mean deviation of the experimental points from this line is 1%. From the thermodynamic properties of the pure substances found in the literature it is possible to calculate ΔH and ΔS values of 26.1 kcal. and 37.3 Gibbs/mole, which compare very well with 25.9 kcal. and 37.2 Gibbs/mole from the above equation. If we further subtract off the contribution of 2HI and I_2 which are known spectroscopically with great precision, we obtain values of ΔH_d and ΔS_d for the dehydrogenations, which agree with calculated values to 0.2 kcal. and 0.2 Gibbs/mole, respectively, over the entire temperature range. It appears that I_2 can be used in this fashion to obtain precise data on many equilibria which are otherwise difficult to observe.

Introduction

Recent investigations in these laboratories of the addition reactions of I_2 ² or HI ^{3a,b} to simple olefins have led to an elucidation of the thermodynamics and kinetics of the reactions of alkyl radicals with HI and I_2 . It was of interest, therefore, to examine the reverse reaction, that is, the homogeneous, gas-phase, dehydrogenation of paraffin hydrocarbon by I_2 which goes to produce the corresponding olefin and HI .

Isobutane was selected as the paraffin, from the viewpoints that: (1) the reaction isobutene + 2HI → isobutane + I_2 was recently studied in these laboratories and found to proceed homogeneously and quantitatively above 200°,³ and (2) isobutane contains a tertiary C-H bond which would be expected to be more reactive than the primary one and so the dehydrogenation reaction would go at an appropriate rate in a convenient temperature range.

As to the gas-phase reaction isobutane + $\text{I}_2 \rightleftharpoons$ isobutene + 2HI, there has been no study of its thermochemistry. In the present study the equilibrium constant of the reaction is measured to ± 3% over a broad composition and temperature range. This, together with thermal data on I_2 and HI , yield data on the free

energy of hydrogenation of isobutene at high temperatures which are accurate to about ± 0.05 kcal.

Experimental

The experimental apparatus was the same as that described in a previous paper.⁴

The concentrations of I_2 and HI were estimated from their optical densities measured by means of a spectrophotometer. The sample beam of a Beckman Model DB spectrophotometer went longitudinally through a quartz glass cylindrical reaction vessel of 364-cc. capacity and 20.0-cm. length placed in an aluminum block furnace. Temperature of the furnace was maintained to within ± 0.2° by an Electrotherm controller in conjunction with a Wheatstone bridge having platinum resistance as one arm of it and the reaction temperature was measured by a copper-constantan thermocouple placed in the reaction vessel.

A tungsten bulb served as a visible light source while a hydrogen lamp was used for an ultraviolet light source. An ethanol-water mixture containing a slight amount of CCl_4 was used as the reference liquid in order to make flat the background of the absorption spectrogram in the region of wave length from 5000 to 2400 Å. The relation between optical densities and concentration was measured at 5000, 4900, 4800, 4600, 4400, 4200, 3000, 2700, 2600, 2500, and 2400 Å. for I_2 , and 3000, 2700, 2600, 2500, and 2400 Å. for HI , respectively, by using silicone oil manometer and Bourdon spoon gage. Up to about 5 mm., I_2 concentration was estimated from the absorption at 4900, 4800, and 5000 Å., and for higher pressure 4600 and 4400 Å. were used. For HI , 2700 and 2600 Å. were used mainly after correcting for the small absorption of I_2 at these wave lengths. From these calibration curves the concentrations of I_2 and HI were estimated with an accuracy of ± 2%. At low concentrations below 1 mm. the background noise contributed an error of about ± 0.02 mm.

(1) (a) This work has been supported by grants from the National Science Foundation and the U. S. Atomic Energy Commission; (b) on leave from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan.

(2) S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962).

(3) (a) A. N. Bose and S. W. Benson, *ibid.*, **37**, 1081 (1962); (b) **38**, 878 (1963).

(4) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).

pressures of I_2 and HI. The reliability of these calibration curves was confirmed by applying them to the kinetic measurements and analysis of the reaction $CH_3I + HI \rightarrow CH_4 + I_2$, which had been kinetically investigated in these laboratories.⁴

The reaction vessel was connected, through greaseless metallic valves, to three lines, one for the pressure gage, one for storing iodine samples, and the other for evacuation and introduction of isobutane. The pressure gage was a conventional all-glass Bourdon spoon gage which was capable of reading 0.5 mm. pressure difference when used as a null-point indicator. Dead space of the spoon and a capillary tubing connecting the spoon to the reaction vessel were heated to $80 \sim 140^\circ$ to prevent the condensation of iodine.

Isobutane, having a specified purity of better than 99.5%, obtained from the Matheson Co., Inc., was distilled trap-to-trap and stored in 5-l. glass bulb, and was distilled again before each run. Iodine used was C.P., obtained from Allied Chem. Co., and was of resublimed quality.

After evacuating the reaction vessel, iodine vapor was sublimed into it up to desired pressure by checking the absorption, and then isobutane was added and the total pressure was measured by the spoon gage and the mercury manometer. The absorptions of I_2 and HI were recorded as a function of time for a period of from 8 to 28 hr., depending on the temperature at which the reaction was to be studied, to allow the attainment of equilibrium. The entire system at the composition attained in the last recorded equilibrium was quickly frozen, by means of liquid nitrogen, into a U-tube which contained auramine-0 to

TABLE I
EQUILIBRIUM DATA FOR THE GAS SYSTEM

$$i-C_4H_{10} + I_2 \rightleftharpoons i-C_4H_8 + 2HI$$

Temp., °K.	Init. press., mm.		Equil. press., mm.				K_p , atm. $\times 10^3$	
	I_2	$i-C_4H_{10}$	I_2	$i-C_4H_{10}$	$i-C_4H_8$	HI	Exptl.	Calcd.
525.1	9.67	200.3	3.24	193.9	6.35	12.7	2.15	2.02
522.5	14.6	119.4	7.82	112.6	6.90	13.8	1.96	1.79
525.7	3.89	275.4	0.33	271.8	3.44	6.88	2.34	2.08
551.9	7.50	206.5	0.88	199.9	6.35	12.7	7.66	6.77
552.5	14.8	121.2	5.25	111.6	9.55	19.1	7.83	6.95
552.5	4.32	158.7	0.26	154.6	3.91	7.82	7.83	6.95
582.7	8.37	131.9	.72	124.3	7.60	15.2	25.8	23.7
582.9	3.56	136.7	.06	133.2	3.42	6.83	26.3	23.9
582.7	5.95	168.8	.26	163.1	5.92	11.8	25.5	23.7

absorb HI. By replacing the coolant from liquid nitrogen to ice-water the volatile fractions consisting of unreacted isobutane and product isobutene were separated and their ratio was estimated by gas chromatography.

TABLE II
THERMODYNAMIC PROPERTIES

Temp., °K.	$K_p \times 10^3$, atm.	ΔF , kcal.		$\Delta H_{(2HI - I_2)}$, kcal.	$\Delta S_{(2HI - I_2)}$, Gibbs/mole	$\Delta F_{(2HI - I_2)}$, kcal.	ΔF_d , ^c kcal.	
		Obsd.	Calcd. ^b				Obsd.	Calcd.
525.7	2.21	6.39		-1.29	39.36	-21.98	28.34	28.43
	2.28	6.35						
	2.34	6.33						
	Av. 2.28	Av. 6.36	6.45					
Calcd. ^a	2.30							
552.5	7.86	5.32		-1.15	39.62	-23.04	28.36	28.49
	7.83	5.32						
	7.83	5.32						
	Av. 7.84	Av. 5.32	5.46					
Calcd. ^a	7.66							
582.7	25.8	4.23		-0.98	39.91	-24.24	28.47	28.57
	26.1	4.22						
	25.5	4.25						
	Av. 25.8	Av. 4.23	4.32					
Calcd. ^a	26.1							

^a Calculated using eq. 1. ^b Calculated using A.P.I. data. ^c $\Delta F_d = \Delta F_{i-C_4H_8} - \Delta F_{i-C_4H_{10}}$.

From the stoichiometric relations, the amount of isobutene produced is equal to the amount of isobutane consumed, and the HI produced is equal to twice the I_2 consumed. These material balances were always better than 4%.

Results and Discussion

Table I gives the results of experiments covering the temperature range from 522.5 to 582.9°K. The

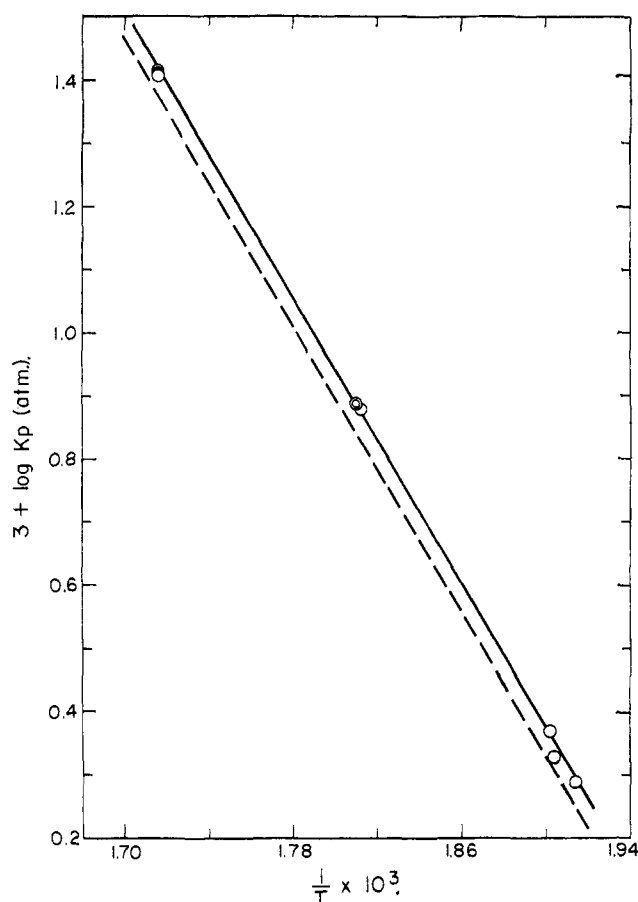


Fig. 1.—Plot of $\log K_p$ vs. $1/T$ for the reaction isobutane + $I_2 \rightleftharpoons$ isobutene + 2HI. Dotted line shows the calculated K_p values from thermodynamic data.

plot of $\log K_p$ vs. $1/T$ gives a good straight line as shown in Fig. 1. The equilibrium constant, K_p of the reaction $i-C_4H_{10} + I_2 \rightleftharpoons i-C_4H_8 + 2HI$ can be calculated

from the thermodynamic data for the reactants and products.⁵ Using these data, K_p values at the experimental temperatures are calculated and listed in the last column of Table I and also are shown as a dotted line in Fig. 1. The two lines in Fig. 1 are almost parallel

(5) See N.B.S. Circular No. 500, A.P.I. Compilation, and JANAF Thermodynamic Data.

TABLE III

 ΔH AND ΔS FOR OVER-ALL REACTION AND FOR THE DEHYDROGENATION PART

Temp., °K.	$-\Delta H_{\text{over-all}}$, kcal.—		$\Delta S_{\text{over-all}}$, Gibbs/mole		$-\Delta H_d^a$, kcal.—		$-\Delta S_d^b$, Gibbs/mole	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
525.7	25.9	26.1	37.2	37.3	27.2	27.4	2.2	2.1
552.5	25.9	26.1	37.2	37.3	27.1	27.3	2.4	2.3
582.7	25.9	26.1	37.2	37.3	26.9	27.1	2.7	2.6

^a $\Delta H_d = \Delta H_{i-C_4H_8} - \Delta H_{i-C_4H_{10}}$. ^b $\Delta S_d = \Delta S_{i-C_4H_8} - \Delta S_{i-C_4H_{10}}$.

to each other, but the experimental K_p values are from 6 to 12% higher than those calculated.

Being given a small correction, each K_p value is recalculated to a common temperature and listed in Table II. The free energy changes of the reaction calculated from the K_p values are shown in the third column and these values, ΔF_{obsd} , are about 0.1 kcal. smaller than ΔF_{calcd} values which are calculated from thermodynamic data of the reactants and products.

From the average values of ΔF_{obsd} at the common temperatures, ΔH and ΔS of the reaction are found to be 25.9 ± 0.3 kcal. and 37.2 ± 0.6 e.u., respectively. The errors indicated are estimated from the accuracies of the quantities determined. These values of ΔH and ΔS give the following equation as the best fit of the experimental K_p values

$$\log K_p(\text{atm.}) = -(25900 \pm 300)/4.575T + 8.130 \quad (1)$$

In Table II we list the value of K_p calculated from this equation. The mean deviation from the average observed values is $\pm 1\%$.

The thermodynamic quantities corresponding to $2\text{HI} - \text{I}_2$ are calculated from those of HI and I_2 and given in the 5th, 6th, and 7th columns. From ΔF_{obsd} for the reaction and $\Delta F_{(2\text{HI} - \text{I}_2)}$, $\Delta F_{i-C_4H_8} - \Delta F_{i-C_4H_{10}}$ (we define as ΔF_d) is determined and shown in the 8th

column. On the other hand, ΔF_d can be calculated directly from the thermodynamic data for $i-C_4H_8$ and $i-C_4H_{10}$. Comparing these ΔF_d values, the temperature dependence is almost identical for both observed and calculated. The observed values are about 0.10 kcal. higher than calculated ones. Although we feel that this is outside our own experimental error, it is well within the limit of error of the A.P.I. data.

In Table III we list the values of ΔH and ΔS calculated from the A.P.I. data along with the results of eq. 1. As can be seen, there is no temperature dependence for either in the range of interest and the results agree to within 0.2 kcal. for ΔH and 0.1 Gibb/mole for ΔS . The 3rd, 4th, 5th, and 6th columns of Table III show similar comparison with the ΔH_d and ΔS_d . The agreement between observed and calculated values are quite extraordinary.

Since the thermodynamic values for HI and I_2 are well known, the present technique gives values for the difference in entropies and enthalpies of any suitable paraffin and its related olefin in a temperature range where such data are either of poor precision or in many cases nonexistent. We hope to extend this technique to studies of other paraffin-olefin systems, to secondary alcohol-ketone systems, and to olefin-diolefin equilibria.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

The Electric Moments of Two Dibenzobicyclooctadienes and Derivatives

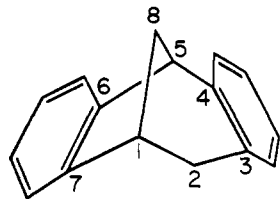
BY DENNIS D. TANNER AND THEODORE S. GILMAN

RECEIVED APRIL 30, 1963

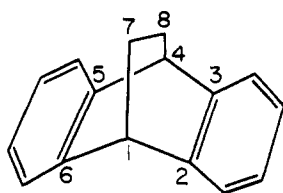
The dipole moments of dibenzobicyclo[2.2.2]octadiene, dibenzobicyclo[3.2.1]octadiene, and some derivatives of the latter have been measured. These moments are compared with those calculated from theoretical models and tend to confirm the configurations assigned on the basis of chemical evidence. The Guggenheim-Smith method of calculating dipole moments from experimental data is compared with the Halverstadt-Kumler method.

Introduction

In the mechanism studies described by Cristol, Arganbright, and Tanner,^{1,2} the hydrocarbons, dibenzobicyclo[3.2.1]octadiene (I) and dibenzobicyclo[2.2.2]octadiene (VIII) (hereafter referred to as ethanoanthracene), and various chloro and hydroxy derivatives of the former were prepared. In addition to the



I



VIII

structural information deduced by them from chemical and kinetic evidence, it was desirable to have further supporting evidence for the assignment of configura-

tions to certain of the derivatives of I. A study of the electric dipole moments of the compounds was therefore undertaken. Furthermore, the bicyclic nature of these molecules gives rise to fairly rigid structures and thus makes possible the estimation of theoretical moments to compare with the experimental ones. This paper presents the experimental results of the dipole moment investigation and an attempt to calculate the moments from assumed models of the molecules studied.

Experimental

Materials.—The syntheses and properties of the compounds studied are described elsewhere.^{1,2} Reagent grade benzene which had been refluxed over CaH_2 and fractionally distilled was used as the solvent for the compounds in the dielectric and refractometric measurements.

Apparatus.—The dielectric constants were measured with a heterodyne-beat apparatus similar to that described by Chien.³ The variable oscillator was tuned with a precision capacitor (General Radio, Type 722-MD) for which a wormgear correction curve had been determined throughout its scale (0–1050 scale divisions). The change in capacitance caused by connecting the dielectric constant cell into the circuit or by changing the contents of the cell could be read with an uncertainty of ± 0.05

(1) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(2) D. D. Tanner, Ph.D. Thesis, University of Colorado, 1961.

(3) J. Chien, *J. Chem. Educ.*, **24**, 494 (1947).