TABLE III

THE HEATS OF FORMATION OF COMPOUNDS INVOLVED AND THE HEATS OF REACTIONS CONSIDERED

Compound	ΔH_{298}, kcal./mole	Reference	Reaction
O_2F_2	+4.73 ± 0.3	25	$O_2F_2 + ClF \rightarrow ClF_3 + O_2 + 30.1$ kcal.
ClF	-13.510 ± 0.11	26	
ClF_3	-38.869 ± 1.0	26	
BrF	-20	27	$2O_2F_2 + BrF \rightarrow BrF_5 + 2O_2 + 95.7$ kcal.
BrF_3	-64.8	28	$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2 + 46.1$ kcal.
BrF_5	-106.2	28	
SF_4	-171.7 ± 2.5	29	$O_2F_2 + SF_4 \rightarrow SF_6 + O_2 + 121.5$ kcal.
SF_6	-288.5 ± 0.7	26	
H_2S	-4.815	26	$4O_2F_2 + H_2S \rightarrow SF_6 + 2HF + 4O_2 + 432.9$ kcal.
HBr	-8.66 ± 0.05	26	$3O_2F_2 + HBr \rightarrow BrF_5 + HF + 3O_2 + 176.9$ kcal.
HCl	-21.97 ± 0.09	26	$2O_2F_2 + HCl \rightarrow ClF_3 + HF + 2O_2 + 91.5$ kcal.
HF	-65.14 ± 0.03	26	

their intermediate product, O_2BrF_5, has only a transitory existence. Still more difficult to control were the reactions with SF_4 and H_2S, with the result that in most cases the analogous intermediate, O_2SF_6, did not form. These facts are in agreement with the amounts of energy

(25) A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc., 81, 6398 (1959).

(26) JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., 1960.

(27) H. Brodersen and H. J. Schumacher, Z. Naturforschung, 2a, 358 (1947).

(28) L. Stein, J. Phys. Chem., 66, 288 (1962).

(29) DuPont's Information Bulletin: "Sulfur Tetrafluoride Technical."

evolved: the more energy liberated, the more difficult it is to quench the reaction and to freeze and stabilize the intermediate compound.

The heats of formation of the compounds involved and the heats of reactions to be considered are given in Table III.

It can be seen that the reactions of O_2F_2 with ClF and HCl evolve the smallest amounts of energy. In fact, it is much easier to slow down these reactions and obtain the intermediate product O_2ClF_3. More energy is evolved in the reactions with bromine fluorides and HBr and they are more difficult to control. Still higher amounts of energy are liberated in the reactions with sulfur compounds and attempts to obtain the intermediate O_2SF_6 failed in most cases.

Performing these reactions at lower temperatures for longer times may give better results.

In the experiments described in this paper, the reactions were carried out for only a few hours at temperatures up to 130–140°K. Since the ΔH's of most of the expected reactions are high, much could be gained if the reactions were carried out at lower temperatures over periods of days or weeks. A series of such reactions has been started. It is found that O_2F_2 reacts with ClF even at 90°K., although the reaction proceeds very slowly. The formation of the violet compound was noticed only after 3 days. The amount of the colored intermediate product seems to increase with time. A further study of the O_2F_2 + ClF reaction and of the reaction of O_2F_2 with other reactants at 77° and 90°K. for long periods of time is planned.

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

The Iodine-catalyzed, Positional Isomerization of Olefins. A New Tool for the Precise Measurement of Thermodynamic Data[1]

BY SIDNEY W. BENSON AND A. N. BOSE

It is shown that in the temperature range of 200–300°, small amounts of I_2 will bring about relatively rapid positional as well as geometrical isomerization of olefins in a homogeneous gas phase reaction. There is no other chemical reaction in the system. Applied to butene-1 and -2 this permits very precise measurements of the equilibrium constants and hence the free energy differences. For the reactions butene-1 ⇌ trans-butene-2 (IV) and cis-butene-2 ⇌ trans-butene-2 (V) it is found that at 508°K., $K_{IV} = 3.48$ and $K_V = 1.63$. The less accurate values estimated from the API tables are $K_{IV} = 4.58$ and $K_V = 1.74$. Using K_{IV} values at 300° we calculate $\Delta H_{IV} = -3.1 ± 0.2$ kcal./mole, $\Delta S_{IV} = -3.6 ± 0.4$ e.u. These are appreciably different from the API values of -2.7 kcal./mole and -2.2 e.u. It is proposed that the API values of the entropy of butene-1 be raised by 1.4 e.u. The values of ΔH_V and ΔS_V are in excellent agreement with API values. It is suggested that the I_2 catalysis in addition to providing a valuable tool for olefin synthesis may also be used to obtain in a relatively simple manner very precise values of the differences in thermodynamic properties of olefins and their parent hydrocarbons. The application to keto–enol equilibria and other unsaturates may also be possible.

Introduction

The reaction of organic iodides (RI) with HI goes stoichiometrically to yield RH + I_2 in the temperature range 250–320°.[2a,b]

$$RI + HI \rightleftharpoons RH + I_2 \qquad (I)$$
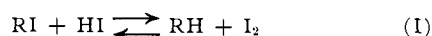
The mechanism of the reaction is atomic, proceeding through an I-atom attack on RI[2]

(1) This work has been supported by Grants from the U. S. Atomic Energy Commission and the National Science Foundation.

(2) (a) R. A. Ogg, J. Am. Chem. Soc., 56, 526 (1934); (b) S. W. Benson and H. E. O'Neal, J. Chem. Phys., 34, 514 (1961).

$$I + RI \underset{2}{\overset{1}{\rightleftharpoons}} R + I_2$$

$$R + HI \underset{4}{\overset{3}{\rightleftharpoons}} RH + I \qquad (II)$$
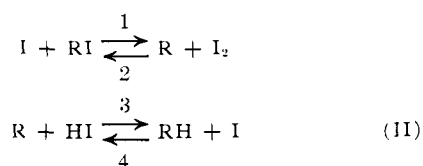
For the saturated hydrocarbons, step 4 is very slow in the above temperature range so that reaction I goes to essential completion (>99%). For the unsaturated hydrocarbons with α-H atoms, the allylic resonance interaction reduces the α(C–H) bond energy by

about 15 kcal. so that the equivalent of step 4 for this α-H atom abstraction will be $\sim 10^7$ times faster than for an alkane in the same temperature range. As a result of this allylic resonance one would expect olefins with α-H atoms to be in labile equilibrium with allyl radicals when exposed to I_2 vapor

$$I_2 \rightleftarrows 2I$$

$$>C=C<_{CH} + I \rightleftarrows >C \cdots C<_C + HI \quad (III)$$
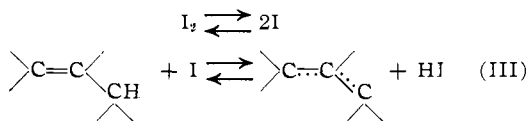
The reverse of reaction III would be expected to form the isomeric olefin. The competing reaction with I_2 which would produce the corresponding allyl iodide $+ I$ would tend to build up a negligible steady state concentration of $RI + HI$, since the equilibrium constant for this process (eq. I) is just as unfavorable as for the alkyl iodides.

Independent studies of the rates of reaction of HI with olefins[3] to form alkyl iodides indicate that these reactions would be negligibly slow in systems containing olefins and I_2. The result is that one could expect that the addition of I_2 vapor to olefin at about 200° would lead to the formation of an equilibrium mixture of all possible isomers but otherwise, no net chemical reaction.[4] From the rate studies in such a system one could expect to get direct data on the magnitude of the allylic resonance energy which is at present uncertain. These we shall report independently.

In the present paper we shall describe our study of the equilibrium system using butene-1 and butene-2 as starting materials. The importance of such studies is that they provide very precise measurements of the differences in free energies of the olefins at temperatures where these differences are not well known. In addition, they provide a tool of possible synthetic value for the production of isomeric olefins.

Experimental

Materials.—Research grade butene-1 and butene-2 supplied by the Matheson Company were further purified by distillations under vacuum and stored in a flask. Analysis of a sample by g.l.c. (gas–liquid chromatography) on a Perkin–Elmer type R-column (polyethylene glycol), V-column and a J-column (silica gel) did not show peaks for any impurities in excess of 0.01 mole %.

Reagent grade iodine was used after distillations.

Experimental Procedure.—The equilibrium measurements were made using a standard type vacuum line and a static method. Reactions were carried out in a Pyrex glass cylindrical vessel placed in an aluminum block furnace. The temperature of the furnace was maintained to within ±0.1° by an Electronotherm controller in conjunction with a Wheatstone bridge with a temperature-sensitive arm of platinum wire having a resistance of 90 ohms. The furnace was insulated with glass wool and mounted in a transite box.

Iodine was first admitted in the vessel and then the butene. The pressures of both were measured by means of a calibrated Bourdon spoon gage fitted with a lamp and scale arrangement. Sensitivity was ±0.15 mm.

That no iodine was consumed in the reaction was confirmed by the fact that the pressure of iodine before and after the reaction in the vessel was the same. No pressure change could be detected during the reaction. This, together with the fact that except for cis- and trans-butene-2 no other products were formed (as observed from g.l.c. analysis) showed that the reaction is exclusively
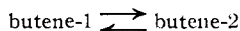
$$\text{butene-1} \rightleftarrows \text{butene-2}$$

In order to find out the equilibrium concentrations of butene-1 and butene-2 (cis and trans), mixtures of iodine and butene-1 were admitted in the reaction vessel and sufficient time was given to establish equilibrium. The mixtures of butene-1 and -2 after separation from iodine were analyzed by g.l.c. (R-column and V-column). Equilibrium concentrations of butenes were

(3) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **37**, 1081 (1962); other papers in press.

(4) The geometrical isomerization produced by iodine atoms occurs at a much faster rate, presumably by the direct addition of I to the double bond.

then calculated quantitatively within ±2%. Results obtained are given in Table I.

The accuracy of the g.l.c. analysis was checked by preparing standard mixtures of the butenes in the high vacuum system (using $P-V-T$ relations to meter the gases) and then analyzing them under similar conditions by g.l.c. The results of these two independent measurements agreed to within about ±2%. The V-column used was 2 ft. long and was operated at 25°. With the He flows used the retention times (measured from air peak) for butene-1, trans-butene-2 and cis-butene-2 were 3.1, 4.1 and 4.8 minutes, respectively. The three were completely resolved.

Also in Table I are given the values of the equilibrium constants for the processes

$$\text{butene-1} \rightleftarrows \text{trans-butene-2} \quad (IV)$$

$$\text{cis-butene-2} \rightleftarrows \text{trans-butene-2} \quad (V)$$
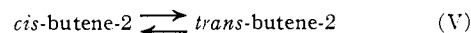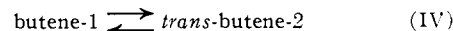
In some of the runs at lower I_2 concentrations true equilibrium for reaction IV was not reached, but in all runs it appears that the cis–trans equilibrium (reaction V) was always maintained. The time in these experiments was about 3 to 18 hours. To demonstrate the reversibility of the system we made three runs in which the starting material was butene-2. As can be seen in Table I, the results are in excellent agreement.

TABLE I
COMPOSITION OF EQUILIBRATED MIXTURES OF BUTENES

Temp., °C.	Time, min.	Starting compd. and press., mm. Butene[a]	I_2	Final equilibrium ratios[b] $K_{IV} = B_{2t}/B_1$	$K_V = B_{2t}/B_{2c}$
234.8	240	(1) 43.9	12.3	3.30	..
	360	(1) 53.4	12.3	3.20	..
	1020	(1) 55.4	11.9	3.70	1.67
	720	(1) 29.7	9.0	3.36	1.58
	40	(1) 49.3	25.7	..	1.67
	195	(1) 54.2	30.1	..	1.71
	95	(1) 29.7	20.6	..	1.62
	40	(1) 96.4	28.8	..	1.60
	40	(1) 28.8	5.4	..	1.60
	180	(1) 45.1	7.5	..	1.60
	95	(1) 45.0	7.5		1.59
			Av.	3.39	1.63 ± 0.02
			Calcd.[c]	4.58	1.74
234.8	360	(2) 38.7	23.2	3.60	1.65
	240	(2) 64.4	19.9	3.56	1.64
	720	(2) 52.1	16.6	3.58	1.64
			Av.	3.58	1.64
			Calcd.[c]	4.58	1.74
300.2	120	(2) 50.7	15.9	2.42	1.55
	360	(2) 68.8	12.6	2.49	1.55
			Av.	2.46	1.55
			Calcd.[c]	3.44	1.67

[a] Number in parentheses refers to position of double bond. [b] See text: K_{IV} = trans-butene-2/butene-1; K_V = trans-butene-2/cis-butene-2. [c] Calculated from values given in API Tables (see footnote, Table II).

Because the enthalpy changes in reactions IV and V are so small, it was not felt worthwhile to make many measurements over any extended temperature range. At lower temperatures, the time to reach equilibrium would be too long, while even at 300° K_{IV} would have only decreased by 25% while K_V would be expected to change by only 6%. This is illustrated by the two runs shown in Table I for $T = 300.2°$.

From the values of K_{eq} listed in Table I we can calculate the respective values of ΔF. These are listed in Table II along with the values calculated from the API Tables. From the temperature variation of ΔF over the range we can compute values of ΔH and ΔS for the isomerization process at the mean temperature of 540°K. These are also listed in Table II along with the API values. Also listed are our own estimated precisions.

Discussion

For the cis–trans isomerization, reaction V, all the values obtained are in excellent agreement with the estimated values from the API Tables. The discrepancy is 0.09 kcal./mole in ΔF_V, which is well within the errors of the API values which we estimate to be

TABLE II

VALUES OF THE THERMODYNAMIC FUNCTIONS FOR BUTENE ISOMERIZATIONS

	butene-1 ⇌ trans-butene-2			cis-butene-2 ⇌ trans-butene-2	
	ΔF_{IV} (508°K.), kcal./mole	ΔF_{IV} (573°K.), kcal./mole		ΔF_V (508°K.), kcal./mole	ΔF_V (573°K.), kcal./mole
Obsd.	-1.26 ± 0.06	-1.03 ± 0.06	Obsd.	-0.50 ± 0.01	-0.50 ± 0.01
Calcd. [a]	-1.70	-1.57	Calcd. [a]	-0.59	-0.59
	ΔH_{IV} (540°K.)			ΔH_V (540°K.)	
Obsd.	-3.1 ± 0.2	(-2.92) [b]	Obsd.	-0.50 ± 0.20	(-0.53) [b]
Calcd. [a]	-2.66		Calcd. [a]	-0.60	
	ΔS_{IV} (540°K), e.u.			ΔS_V (540°K.) e.u.	
Obsd.	-3.6 ± 0.4	(-3.1) [b]	Obsd.	0.00 ± 0.4	(0.14) [b]
Calcd. [a]	-2.18		Calcd. [a]	0.00	

[a] All calculated values are from API Tables. The values of API Tables show a discrepancy of 0.2 kcal. in ΔF_{IV} calculated from their free energy tables or from the separate ΔH_{IV}, ΔS_{IV} tables. We have chosen the latter. [b] Observed by Voge and May (ref. 6) at an average $T \sim 440°K$.

about ± 0.2 kcal./mole. Our own observed values are probably more accurate.

For reaction IV (butene-1 → trans-butene-2) our values of ΔF_{IV} are consistently lower in magnitude than the API values by about 0.5 kcal./mole. This is probably within the limits of error of the API values which we estimate at about ± 0.6 kcal./mole. Our ΔH_{IV} value is about 0.4 kcal./mole more negative than the API value which again is probably within the limits of precision of the latter. However, the discrepancy on the ΔS_{IV} is 1.4 e.u., a rather large value. Since we believe that our direct observations are not in error by more than ± 0.4 e.u. we feel that this rather large discrepancy must arise from errors in the API values. The API values are obtained from smoothing experimental third law data on C_p down to low temperatures together with statistical mechanical estimates. The errors in the former are at least ± 0.3 e.u. or more if low temperature transitions have been lost or if crystallization is imperfect.[5] This would place a lower limit of about ± 0.5 e.u. on the uncertainty in ΔS_{IV}. Unfortunately, no meaningful limits can be placed on the statistical calculations because of the lack of unique vibrational assignments and barrier assignments for the hindered rotations.

Since the third law measurements usually give minimum values for the entropies it is unlikely that the butene-2 entropies are in error. Consequently we feel that the discrepancy of about 1.4 e.u. lies in the butene-1 value and we would propose that its entropy be raised by this amount.

Voge and May[6] studied the same gas phase isomerization of butene-1 to cis- and trans-butene-2 in the presence of two solid catalysts, (a) silica-alumina-magnesia gel and (b) "porocel" (bauxite). Their

(5) J. G. Aston, et al., J. Am. Chem. Soc., **68**, 52 (1946), had great difficulty in crystallization of butene-1 and estimated 3.0 e.u. as the residual entropy of the initial glass.

(6) H. H. Voge and N. C. May, ibid., **68**, 550 (1946).

values of ΔH and ΔS for the two reactions are shown in Table I in parentheses and are in much better agreement with our own data than with the API data. It is interesting to note that they did not have sufficient confidence in their own values to emphasize the discrepancies with the available data, particularly on ΔS_{IV}.

If the butene system can be used as a criterion, it appears as though the I_2-catalyzed positional isomerization of olefins may provide a very powerful tool for the measurement of free energy differences between isomeric species. The precision of measurement of ΔF is of the order of 0.05 kcal. at 500°K. This is about a factor of 10 better than the methods currently available of taking differences in entropies from third law measurements together with differences in heats of reaction (combustion or hydrogenation) and extrapolating to high temperatures. In particular it circumvents completely the very difficult problem of first obtaining compounds of extremely high purity.

The present method may be extended to relating the olefins to the parent hydrocarbon via the equilibrium

$$R_1R_2CH\text{-}CHR_3H_4 + I_2 \rightleftarrows R_1R_2C\text{=}CR_3R_4 + 2HI$$
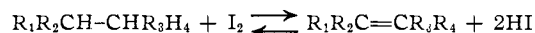
Using large amounts of alkane ($R_1R_2CH\text{-}CHR_3R_4$) and small amounts of I_2, the equilibrium proceeds far enough to give easily measurable amounts of olefin and HI and with good precision. We are currently engaged in studies of a number of such systems. Very appealing is the prospect that similar equilibria in other systems as keto–enol equilibria may be measurable by these techniques.

Where the differences in enthalpy are in excess of 3 kcal., then the measurement of K at two different temperatures will permit the calculation of ΔH and ΔS with precisions of ± 0.1 kcal. and ± 0.2 e.u., respectively. The use of photochemically generated iodine atoms may permit extending this technique to lower temperatures.