The Kinetics and Mechanism of the Reaction of Iodine with Tetrahydrofuran. A Carbon-Hydrogen Bond Dissociation Energy in Tetrahydrofuran[1a]

F. R. Cruickshank[1b] and S. W. Benson

Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025. Received October 12, 1968

Abstract: The reaction of iodine (3.4–16.6 torr) with tetrahydrofuran (THF) (6.6–330.6 torr) has been studied over the temperature range 500–633°K in a static system. The data are explained on the basis of the initial abstraction of a hydrogen atom by iodine being the rate-determining step. Initially significant surface effects were minimized by teflonizing the reaction vessel. The rate constant, k_1, for eq 1 (see text) is given by log k_1 (M^{-1} sec^{-1}) = 11.67 ± 0.5 − [(21.5 ± 1.3)/θ], where θ = 2.303RT in kilocalories/mole, the errors quoted being 95% confidence limits. With the assumption that the α C–H bond is the weaker, and that $E_{-1} = 1$ kcal/mole, the above result yields a bond dissociation energy $D°(C–H) = 91.5 ± 1.5$ kcal/mole, and a π-bond energy in 2,3-dihydrofuran of 59 kcal/mole. It is estimated that the same bond energy relations hold true in the open-chain vinyl ethers.

There are very few data on carbon–hydrogen bond dissociation energies of ethers and none whatsoever on cyclic ethers. It is of interest, therefore, to extend to the cyclic ethers previous work[2-4] on iodine reactions with oxygen-containing compounds which yield bond dissociation energies. The present paper deals with the reaction of iodine with tetrahydrofuran in order to examine the effect of the oxygen atom on the C–H bond strength. In the case of dimethyl ether,[4] the C–H bond was weaker than that of primary alkanes by 4.7 kcal/mole.

Experimental Section

Apparatus. The spectrophotometrically monitored reaction vessel has been described previously[5] as has the packed vessel.

Materials. I_2 (Mallinkrodt) was resublimed and degassed at liquid nitrogen temperature prior to use. Tetrahydrofuran (Mallinkrodt), 2,5-dihydrofuran, and furan (Eastman Kodak) were degassed at liquid nitrogen temperature and freshly distilled *in vacuo* before each run. Purity of the tetrahydrofuran and furan was assessed by nmr and glpc and was better than 99.5%. HI (Matheson) was degassed at liquid nitrogen temperature and distilled into a blackened storage bulb. The HI was further degassed and distilled prior to each run.

Procedure. The run procedure was similar to that previously described[4] and the reaction was monitored at 445, 280, 260, and 235 mμ.
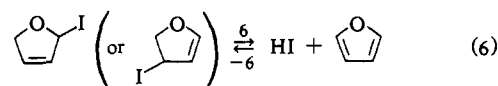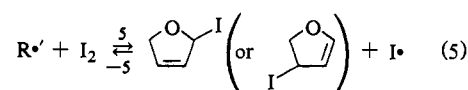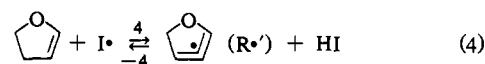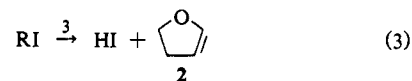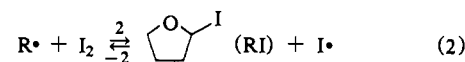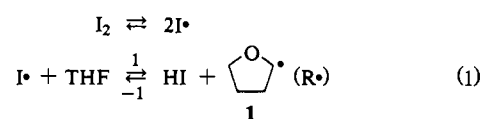
Product analyses were performed by low-temperature (−40 to −50°) nmr spectroscopy, in addition to the Cary 15 spectrometer.

Results

It was found that the initial rate of disappearance of iodine $-(d[I_2]/dt)_i$ was first order in tetrahydrofuran and one-half order in I_2. This order dependence (Table I) was obeyed, reproducibly only in a teflonized reaction vessel. The data for all runs are listed in Table I. Over the initial stages, $-2(d[I_2]/dt)_i = d[HI]/dt$ within ±7%

and the yield of HI = $2\Delta[I_2]$ within ±5%. The only detected hydrocarbon products were furan and some polymer. Nmr provided a very sensitive test for the total absence of 2,5-dihydrofuran and aldehydic protons. A singlet at τ 1.7 and a triplet at τ 6.75 were attributed to polymer. In keeping with the absence of aldehydes, no noncondensable gases were detected. If the ring opened, it would result, initially, in an acyl iodide with an iodine on the terminal carbon atom, also. This could eliminate HI to give an iodoketene which would undoubtedly polymerize to give an iodo-substituted polymer.

Since no iodide absorption was detected in the uv spectrum of the products, and on the assumption that the α C–H bond is the weaker, the following mechanism is proposed.

The short-wavelength optical density data were inconsistent with the presence of any iodide, unless its absorption coefficient was very low. This would be contrary to previous experience[4] where iodomethyl methyl ether has

(1) (a) This work has been supported in part by Grant No. AP 00353-04 from the Department of Air Pollution, Public Health Service; (b) Postdoctoral Research Associate.
(2) R. Walsh and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 4570 (1966).
(3) F. R. Cruickshank and S. W. Benson, *J. Phys. Chem.*, in press.
(4) F. R. Cruickshank and S. W. Benson, *Intern. J. Chem. Kinetics*, in press.
(5) R. Walsh and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 3480 (1966).

Table I. Kinetic Runs

Run	THF$_i$, torr	I$_{2,i}$, torr	$(d[I_2]/dt)_i$, torr/sec $\times 10^3$	Temp, °K	k_1, M^{-1} sec^{-1} $\times 10^{-2}$
1	148.1	7.36	44.6	559.9	18.3
2	74.2	7.55	26.0	559.9	20.2
3	190.2[a]	9.50	43.8	545.4	20.8
4	114.1[a]	6.68	47.0	545.4	41.8
5	244.1	15.9	7.5	515.5	4.75
6	40	16.60	1.7	515.5	6.40
7	28.6	11.6	1.16	515.5	7.30
8	18.9	18.2	1.21	515.5	9.20
9	80.6	13.2	1140	631.2	111
10	69.2	11.4	1140	631.2	138
11	60.32	9.88	984	631.2	147
12	53.25	8.75	878	631.2	158
13[b]	13.95	14.65	132.2	604	131
14	11.65	12.35	99.5	604	128
15	9.72	9.9	80.7	604	140
16	7.68	7.67	141	620.7	239
17	6.62	6.63	109	620.7	231
18	117.6	11.98	1.47	507.4	2.86
19	330.6	9.22	3.13	505.7	2.62
20	158.5	9.43	1.73	505.8	2.99
21	228.3	16.2	75.5	552.7	16.1
22	128.13	6.93	27.9	552.7	16.3
23	138.2	7.33	31.2	552.7	16.4
24	83.3	9.1	22.1	552.7	17.2
31[c]	11.47	5.68	216	632.6	220
32	9.65	4.8	171	632.6	226
33	8.18	4.05	112	632.6	190
34	6.82	3.38	102	632.6	226

[a] Runs in packed vessel. [b] Runs 13–24, in teflonized vessel, first series. [c] Runs 31–34, in teflonized vessel, second series.

an abnormally high absorption coefficient. The absorption at 280–235 mμ was consistent with the production of furan, but its very small absorption coefficient precluded accurate analysis.

The over-all stoichiometry of this reaction is given by

$$\text{THF} + 2\text{I}_2 \rightarrow 4\text{HI} + \text{(furan)}$$
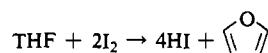
The iodine mass balance supports this, but the pressure increase, ΔP, which should be equal to $-\Delta[\text{I}_2]$ varied between 90 and 17% of this value. Accurate measurement of ΔP could be achieved only by backing argon, at the initial pressure of the reactants, up to the closed reactor stopcock, opening it, and observing ΔP on the Pace pressure transducer. This operation takes some time to set up, so that values of ΔP could not be obtained in the initial stages. The procedure was necessary because tetrahydrofuran dissolved rapidly in the silicone stopcock grease. The discrepancy in ΔP was attributed to the formation of the observed polymer.

The rate-determining step of the reaction was attributed to step 1, and the rate was equated to $-\frac{1}{2}(d[\text{I}_2]/dt)_i$. The rate constant of step 3 may be estimated[6] as $10^{13.2-33/\theta}$, where $\theta = 2.303RT$ in kilocalories/mole, whence it may be shown that step 3 proceeds at least 100 times faster than step 1. The order of the reaction is also incompatible with step 3 being rate controlling. In the 2,3-dihydrofuran, the allylic C–H bond will be about

12 kcal weaker than that of THF, so that the rate of step 4 will be much faster than that of step 1. Again, if (4) were rate determining, the observed order of reaction would be inexplicable. Although there is some uncertainty about the thermodynamic parameters estimated in the above analysis, we feel that the errors involved are much smaller than those required to make any reaction, but step 1, rate controlling.

The results obtained are listed in Table I and are shown in Arrhenius form in Figure 1. From Figure 1 the order dependence is seen to be erratic at the low temperatures in the untreated vessel. In the packed vessel, with a sevenfold increase in surface-to-volume ratio, the rate constant increased by up to a factor of 2. To minimize the significance of the heterogeneous component, the reactor was teflonized[7] and the first series of runs performed. The final runs at the highest temperature were then performed and yielded rather lower rate constants. Some surface contribution to the rate was probably still present, therefore, so that the lower set of values was preferred. Order dependence at the lowest temperatures was good in the teflonized vessel.

The least-squares line through only those data obtained in the teflonized reactor is represented by the equation

$$\log k_1 \left(M^{-1} \text{ sec}^{-1} \right) = 12.35 \pm 0.5 - \frac{23.0 \pm 1.3}{\theta}$$

where all error limits quoted in this paper are 95% confidence limits. This A factor is higher than expected, a

(6) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

(7) Described in K. W. Egger and S. W. Benson, *ibid.*, **87**, 3314 (1965).
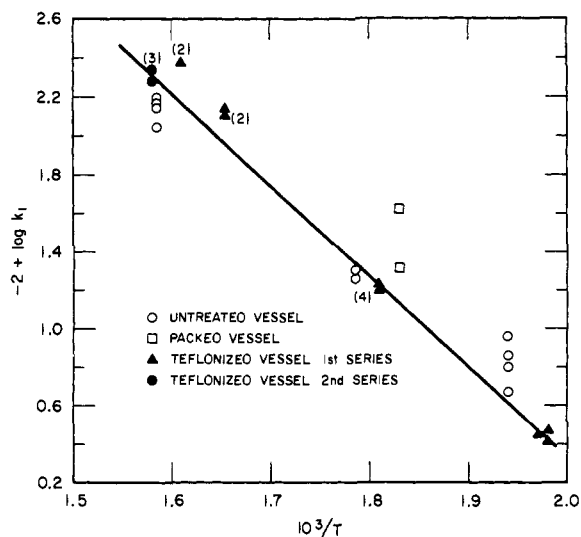
Figure 1. Arrhenius plot: hydrogen abstraction from THF by an iodine atom.

Figure 2. HI inhibition of hydrogen abstraction from THF.
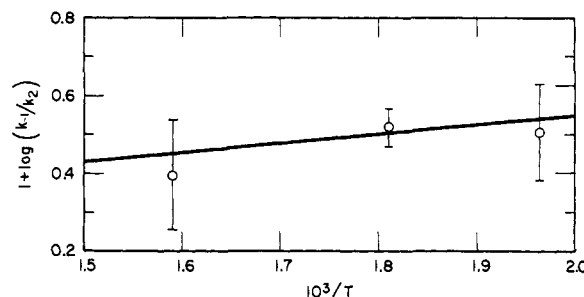
Figure 3. Arrhenius plot: inhibition ratios, k_{-1}/k_2.

value of around $10^{11.3}$ being consistent with the dimethyl ether results[4] in view of the differing number of hydrogen atoms. Since we favor the lower values at the highest temperature, we prefer the best line through these, giving the relation
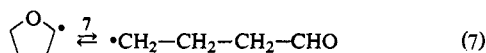
$$\log k_1 \, (M^{-1} \, \sec^{-1}) = 11.72 \pm 0.5 - \frac{21.5 \pm 1.3}{\theta}$$

If we assume that the 3-position C–H bond is ~ 94.5 kcal/mole, a small correction ($\leq 10\%$ of k_1) should be made for the competitive abstraction of these atoms, so that the final relation becomes

$$\log k_1 \, (M^{-1} \, \sec^{-1}) = 11.67 \pm 0.5 - \frac{21.5 \pm 1.3}{\theta}$$

Since there appears to be no entropy or heat capacity data on furans, we have estimated that for reaction 1, $\Delta C_p^\circ = 0.9 \pm 0.5$ gibbs and $E_{-1} \sim 1$ kcal/mole.[8] Accordingly, $DH^\circ_{298}(\text{1-H}) = 91.5 \pm 1.5$ kcal/mole and $\Delta H_f^\circ(1) = -4.6 \pm 1.5$ kcal/mole.

No evidence of ring opening was found, so that we can place a limit to the activation energy of this process.

$$\overset{O}{\underset{}{\bigcirc}}\cdot \; \overset{7}{\rightleftarrows} \; \cdot CH_2-CH_2-CH_2-CHO \qquad (7)$$

It is endothermic by ~ 1.7 kcal/mole, but has an entropy increase of ~ 13.6 eu. The alternative displacement reaction[9] is too endothermic ($\Delta H \approx 21$ kcal) to be significant.

If we assume that the rate of step 7 must be $\leq 1\%$ of step 2 in order that it not be observed

$$10^{-2} \geq \frac{k_7(R\cdot)}{k_2(R\cdot)(I_2)} = \frac{k_7}{k_2[I_2]}$$

$$k_7 \leq 10^{-2} \cdot k_2[I_2] = 10^{-2} \cdot 10^{9.5} \cdot 10^{-3.7}$$

i.e., $k_7 \leq 10^{3.8} \sec^{-1}$. The A factor of step 7 is estimated as $10^{13} \sec^{-1}$ whence the above relation yields
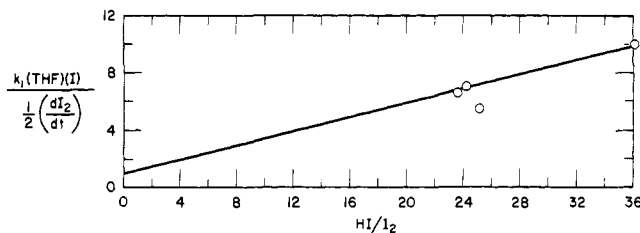
$$3.8 \geq \log A_7 - E_7/\theta$$

i.e., $E_7 \geq 9.2 \times 2.6 \geq 24$ kcal. Thus the intrinsic activation energy ($E_7 - \Delta H_7$) of step 7 is ~ 22 kcal/mole, which is very close to the intrinsic activation energies for the comparable reactions.[10]

$$\overset{}{\underset{}{\bigcirc}}\cdot \rightarrow \overset{}{\underset{}{\bigcirc}} \qquad E_{\text{intrinsic}} = 20 \text{ kcal}$$

$$\overset{}{\underset{}{\bigcirc}} \rightarrow \text{/\!\!/\!\!\!\backslash\!\!\backslash} \qquad E_{\text{intrinsic}} = 24 \text{ kcal}$$
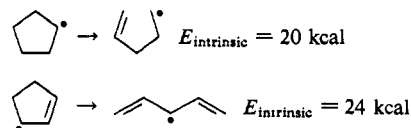
If significant pressures of HI are present in the initial stages of the reaction, the rate expression

$$-\left(\frac{d[I_2]}{dt}\right) = \frac{2k_1[\text{THF}][I\cdot]}{\dfrac{k_{-1}[\text{HI}]}{k_2[I_2]} + 1}$$

must be used, since over the wide range of iodine systems now studied in these laboratories[8] the inhibition ratios ($e.g.$, k_{-1}/k_2, k_{-4}/k_5) do not vary much since $k_4 \sim 10^5 k_1$, so that reaction 4 is not rate controlling even in HI-inhibited runs. Thus, $2k_1[\text{THF}][I\cdot]/-(d[I_2]/dt)_i$ should vary linearly with $[\text{HI}]/[I_2]$.

A series of HI-inhibited runs was made. The experimental results are given in Table II. A plot of this relation, $2k_1[\text{THF}][I\cdot]/-(d[I_2]/dt)_i$, is shown in Figure 2 for runs made at about 629°, where the line is constrained to pass through the point (0, 1). The values of k_{-1}/k_2 calculated from the slopes of such lines, for runs at 509, 553, and 629°, are shown in Arrhenius form in Figure 3. Reproducibility of the measurements was not as high as is customary, and this was attributed to a surface component

(8) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).
(9) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(10) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966).

Table II. HI-Inhibited Runs

Run	$[I \cdot]$, $M \times 10^8$	THF, torr	k_1, $M^{-1} \sec^{-1}$ $\times 10^{-3}$	$(d[I_2]/dt)_i$, torr/sec $\times 10^2$	$[HI]/[I_2]$	Temp, °K
25	10.2	203.8	1.65	4.77	2.08	552.7
26	9.08	207.1	1.65	2.38	3.71	552.7
27	7.48	280.8	1.65	1.89	8.46	552.7
37	2.66	395.9	0.302	0.412	2.32	509.5
38	2.04	302	0.302	0.181	4.77	508.7
39	1.62	334.1	0.302	0.0316	28.3	508.9
41	29.2	15.1	20.9	3.33	25.2	629.2
42	29.4	32.1	20.9	3.92	36.1	630.0
43	45.2	29.24	20.9	7.80	24.2	628.4
44	43.9	17.2	20.9	4.68	23.6	628.9

of the reaction, because HI, I_2, and tetrahydrofuran mixtures react at 100° in the gas phase in a teflonized vessel to produce iodo compounds resulting in a positive ΔP. Measurement of the high-temperature inhibition ratios was, therefore, made less accurate, since only HI and I_2 could be premixed in the mixing vessel, and tetrahydrofuran had to be added to a sample of this mixture in the reaction vessel, where at 630 °K the mixing time must be a significant part of the reaction time. The data of Figure 3 do not warrant a least-squares treatment, the best straight line drawn by inspection, being given by $\log (k_{-1}/k_2) = -0.9 \pm 0.9 + [(1.1 \pm 2.2)/\theta]$. In view of the poor precision, possibly the only conclusion to be drawn from this result is that $E_{-1} - E_2$ is consistent with the usually observed 1 kcal/mole.[8]

Conclusions

The measured bond dissociation energy[11] of 91.5 kcal/mole for the C–H bond in tetrahydrofuran is one of the very few direct measurements of bond dissociation energy in cyclic compounds. The value of 93 kcal/mole cited for cyclopentane comes, in fact, from a study of methyl radical abstraction and application of the alkane-methyl radical, Polanyi relationship.[12] It would appear, if we assume that the activation energy for ring opening by $I \cdot$ is ~ 17 kcal over the endothermicity, that $DH°(C–H)$ of, certainly, cyclopropane and perhaps cyclobutane, cannot be determined by the iodine technique purely because the ring strain is so high. It should, however, be possible to measure the $DH°(C–H)$ of five- to eight-membered alkane rings and cyclic ethers.

The observed $DH°(1\text{-H}) = 91.5$ kcal/mole is ~ 3 kcal/mole lower than that for the secondary C–H in propane and 1.5 kcal/mole lower than the value, deduced from a Polanyi relationship,[12] for cyclopentane. Comparing these results with other oxygenated compounds,[8] we see that an oxygen atom lowers the $DH°(C–H)$ at an adjacent carbon atom by ~ 4 kcal/mole, e.g., as shown in Table III. It seems likely, therefore, that $DH°(C–H)$ in cyclopentane is about 95.0 kcal/mole, although the difference from 4 kcal/mole of Δ in this case is within the error margins involved.

The ring strains in cyclopentane (6.3 kcal/mole)[13] and cyclopentene (5.9 kcal/mole) are comparable, so that it

(11) See S. W. Benson, *J. Chem. Educ.*, **42**, 503 (1965), for the thermodynamic definition of bond dissociation energy, $DH°$.
(12) A. F. Trotman-Dickenson, *Chem. Ind.* (London), 379 (1965).
(13) S. W. Benson, *et al.*, *Chem. Rev.*, in press.

Table III

Bond	$DH°$, kcal/mole	Δ, kcal/mole
CH_3CH_2–H	98	
$HOCH_2$–H	94	4
$(CH_3)_2CH$–H	94.5	
$(CH_3)_2(OH)C$–H	90.2	4.3
$CH_3CH_2CH_2$–H	98.0	
CH_3OCH_2–H	93.30	4.7

may reasonably be deduced that the ring strain of the cyclopentyl radical is very close to 6 kcal/mole. If the same invariance of ring strain is present in the furan ring series, we may calculate[13] $\Delta H_f°_{298}(2) = -21.37$ kcal/mole. The heat of the reaction 8 now enables us to calculate the π-bond energy, $D_\pi°$, in 2,3-dihydrofuran.
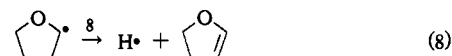
$$\Delta H_8 = -21.37 + 52.1 + 4.6 = 35.3 \text{ kcal/mole}$$

This value of ΔH_8 is merely the $DH°[\beta \text{ C–H}]$ reduced by $D_\pi°(2,3\text{-dihydrofuran})$, i.e.

$$35.3 = 94.5 - D_\pi°(2,3\text{-dihydrofuran})$$

whence $D_\pi°(2,3\text{-dihydrofuran}) = 59.2 \pm 3$ kcal/mole, the same within the error limits as $D_\pi°$(ethylene).

Since methyl vinyl ether will have an identical heat of hydrogenation with 2,3-dihydrofuran, we can estimate $DH°(C–H)$ in methyl ethyl ether as also 91.5 ± 1.5 kcal/mole, and the π-bond energy in the vinyl ether as 59 ± 1.5 kcal/mole. This is based on the reasonable assumption that the $DH°(C–H)$ in the ethyl ether is the same as that in propane, namely 98 kcal/mole.

Oxygen-containing compounds in these studies seem to be associated with surface contributions to the rate. However, in the series dimethyl ether,[4] formaldehyde,[2] methanol,[3] 2-propanol,[5] tetrahydrofuran, and ethylene oxide,[14] only dimethyl ether is relatively free from the problem.

(14) S. W. Benson and F. R. Cruickshank, unpublished results.