liquid 1,2-dichloroethane[26] at 25° is 10.16 and the dipole moment (1.88 D.) is not considerably different from the value in benzene solution. From Table I it is apparent that the dipole moment of this solute decreases in the same manner as those of 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane in the solvent order *p*-dioxane > benzene > *p*-xylene > mesitylene > cyclohexane. For 1,1,2,2-tetrachloroethane the potential barrier to internal rotation is large,[17] and the solvent effect would seem to be due to molecular interaction rather than any increased freedom for intramolecular rotation. From Figures 2–4, although the degree of interaction does appear to be anomalously large, the dipole moment changes for 1,2-dichloroethane are reasonable and suggest that they are not solely due to intramolecular effects.

In a specific solvent increasing molecular interaction appears to be accompanied by increased dipole moment changes for the chloroethane series. However, this effect decreases in the solvent order benzene > *p*-xylene > mesitylene, suggesting that the induced dipole moments decrease with increasing basicity or mean polarizability for these systems.

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(26) F. Buckley and A. A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," National Bureau of Standards, Circular 589, Government Printing Office, Washington, D. C., 1958.

Some Thermochemical Properties of Methyl Vinyl Ether, α-Chloroethyl Methyl Ether, and Iodomethyl Methyl Ether. Evidence for Nonbonded Electrostatic Interactions[1]

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Abstract: The entropies of methyl vinyl ether (MVE, $S°_{298} = 73.5$ gibbs/mole) and α-chloroethyl methyl ether (CME, $S°_{298} = 82.4 \pm 2.1$ gibbs/mole) have been calculated, respectively, by statistical mechanical methods, and from the measured equilibrium constant, K_α, $CH_3OCHClCH_3 \rightleftarrows HCl + CH_3OCH{=}CH_2$ (α). In the latter measurement, HCl pressures were varied from 104.5 to 227.8 torr, and MVE from 28.57 to 213 torr. $\log (K_\alpha/\text{atm}) = [(34.0 \pm 1.5)/4.576] - [(17.5 \pm 0.7)/\theta]$, where $\theta = 2.303RT$ in kilocalories/mole, and errors quoted are 95% confidence limits. Smoothing these values to $\Delta H = 17.0$ kcal/mole by comparison with the similar equilibrium for ethyl vinyl ether leads to $\Delta H_f°_{298}(\text{CME}) = -65.2 \pm 1.2$ kcal/mole. The heat of formation of iodomethyl methyl ether ($\Delta H_f°_{298}(\text{IME}) = -29.3$ kcal/mole) was calculated from the equilibrium constant, K_{eq}, at 566°K for the system $CH_3OCH_3 + I_2 \rightleftarrows HI + ICH_2OCH_3$ (IME) and an assigned value for the entropy of the iodomethyl ether. I_2 pressures were varied from 3.76 to 18.85 torr and dimethyl ether pressures from 39.62 to 592 torr. The temperature range was 515–631.6°K. $S°_{298}(\text{CME})$ was abnormally low by 1.9 gibbs/mole on comparison with isoelectronic *sec*-butyl chloride, and $\Delta H_f°(\text{CME})$ was abnormally stable by about 6.1 kcal/mole. $\Delta H_f°(\text{IME})$ showed a similar enhanced stability of about 3 kcal/mole. Both of these values are shown to be consistent with an electrostatic interaction of the halogens with the terminal methyl group arising from the alternate polarity of bond dipoles.

Data on the entropies and heat capacities of ethers are particularly scarce,[2] only those of dimethyl ether having been calculated[3] by the method of Pitzer and Gwinn[4] from a spectroscopic frequency assignment.

Entropies of other ethers have been estimated by group additivity methods[2] or else by an "isoelectronic replacement rule." The success of this rule depends on the observation that, at 298°K, replacement of the oxygen atom in an oxygen-containing compound by an isoelectronic group, here the methylene group, does not significantly alter the entropy, provided due account is taken of any symmetry changes involved and the very small contribution of the H atoms. Table I shows that the rule is generally accurate within ±1 gibbs/mole. The agreement is expectedly poor for the acids (and presumably esters), which have high OH (or OR) rotation barriers. The poor result for H_2O_2 is due to the large difference in moments of inertia between H_2O_2 and C_2H_6.

The external moment of inertia about the C–C axis in C_2H_6 is three times larger than that about the O–O axis in H_2O_2. This is also approximately the case for the internal rotation, and correction for both of these effects amounts to about 2.5 gibbs/mole. A crude *a priori* estimate of the effect of losing two H atoms in a molecule can be made by assigning one C–H stretch at 3000 cm^{-1} and two H–C–C deformations at about 1000 cm^{-1}. At 300°K these amount to about 0 3 gibbs/mole per H atom, or 0.6 gibbs/mole for two H atoms, in good agreement with most of the ΔS values shown.

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(1) (a) This work was supported in part by Grant No. AP-00353-04, Public Health Service, Division of Air Pollution; (b) Postdoctoral Research Associate.

(2) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, in press.

(3) Z. Seha, *Chem. Listy*, 49, 1569 (1955).

(4) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 10, 428 (1942).

Table I. Comparison of the Intrinsic[a] Entropies ($S°_{int}$) of Isoelectronic Compounds

Compound	(σ, n)[b]	$S°_{298}$	$S°_{int}$	$\Delta S°_{int}$
C_3H_8	(18, 1)	64.5	70.2	0.5
C_2H_5OH	(3, 1)	67.5	69.7	
n-C_4H_{10}	(18, 1)	74.1	79.8	0.7
n-C_3H_7OH	(3, 1)	76.9	79.1	
C_3H_6	(3, 1)	63.8	66.0	0.6
CH_3CHO	(3, 1)	63.2	65.4	
Cyclopropane	(6, 0)	56.8	60.4	0.9
Ethylene oxide	(2, 0)	58.1	59.5	
But-1-ene	(3, 1)	73.8	76.0	0.4
C_2H_5CHO	(3, 1)	73.4	75.6	
Isobutylene	(18, 1)	70.2	75.9	−0.3
Acetone	(18, 1)	70.5	76.2	
C_3H_6	(3, 1)	63.81	66.0	6.6
HCOOH	(1, 1)	59.4	59.4	
C_2H_6	(18, 1)	54.85	60.6	5.0
HOOH	(2, 2)	55.60	55.6	

[a] $S°_{int} = S°_{obsd} + R \ln (\sigma/n)$ in units of gibbs/mole. [b] σ = symmetry number (internal + external), n = number of optical isomers.

The differences in entropies between hydrocarbon[2] and corresponding oxygen compounds will become larger as the temperature is raised, owing to the increased contributions of the C–H vibrational modes with increasing temperature.

In order to generate enough groups for the additivity method[2] and reduce the limits of uncertainty in the entropy of ethers, many more measured values are required, and in the present paper values are derived for methyl vinyl ether (MVE), α-chloroethyl methyl ether (CME), and iodomethyl methyl ether (IME).

Experimental Section

Apparatus. The spectrophotometrically monitored reaction vessel has been described previously[5] as have the procedure and sources of materials for the iodomethyl methyl ether equilibrium.[6]

Materials. CH_3OCHCH_2 and HCl (Matheson) were degassed at liquid nitrogen temperatures and distilled prior to use. Glpc analysis revealed a 5% impurity level in the ether, which seemed to be inert, however.

Procedure. In the determination of the CME equilibrium, HCl was added to methyl vinyl ether in the reactor, the system sealed at the pressure transducer stopcock, the pressure gauge nulled, and the initial pressure noted. The decrease in pressure, $-\Delta P$, was followed on a Pace pressure transducer with a sensitivity of ± 0.02 torr.

Results and Discussion

Methyl Vinyl Ether. The entropy and heat capacity of MVE may be calculated from the recent frequency assignment[7,8] by standard statistical mechanical methods, the only problem being the treatment of the two internal rotors.

The methyl and vinyl rotors have been assigned the frequencies[8] 245 and 205 cm^{-1} observed at 193.2°K. From the frequencies, barrier heights (V) may be calculated from the formula[9]

$$\nu = 3.14n \sqrt{\frac{V}{10^{40} I_{red}}}$$

where I_{red} is the reduced moment of inertia of the rotor in g cm^2, V is in cal/mole, and n is the number of minima in the potential energy curve of the rotor. These barrier heights may then be used in the Pitzer and Gwinn calculation[4] to give the entropy and $C_p°$ contribution of the hindered rotors at any temperature. From the tentative structure[8] of MVE, we calculate I_{red}(vinyl rotor) = 8.1×10^{-40} g cm^2 and I_{red}(methyl rotor) = 4.9×10^{-40} g cm^2. The barrier height for the vinyl rotor is 3.84 kcal/mole, if $n = 3$, this value being preferred since unpublished infrared evidence indicates that *gauche*, rather than *trans*, isomers are the other stable forms of vinyl ethers.[7] For the vinyl rotor the oxygen atom represents the molecular "frame," and n, although not a symmetry number, is treated as one when using the Pitzer–Gwinn tables. Pitzer has shown[10] that, for such an asymmetric rotor, the overall changes in moment of inertia with internal rotation are cancelled by changes in the inertia factor for the normal modes, if such vibrations are classical. However, if the tables set up for a truly symmetric rotor are used, $R \ln n$ must be added to the entropy and free-energy function.[10] Accordingly, we obtain $S°_{298}$(MVE) = 71.3 + $R \ln 3$ = 73.5 gibbs/mole. $S°_{298}$(but-1-ene) is 73.8 gibbs/mole, so that the replacement rule gives a good approximation at 298°K. The six frequencies associated with the two H atoms are roughly 2 at 3000 cm^{-1}, 2 at 1150 cm^{-1}, 1 at 1450 cm^{-1}, and 1 at ~700 cm^{-1}, whence Δ (Table I) is ~0.4 gibbs/mole, and the replacement rule predicts 73.4 gibbs/mole for MVE.

MVE heat capacity data are as follows: 19.0 (298°); 19.1 (300°); 23.7 (400°); 27.7 (500°); 31.1 (600°); 36.1 (800°); 39.9 (1000°); 45.6 (1500°). All values are given in gibbs/mole; temperatures in parentheses are in °K.

α-Chloroethyl Methyl Ether (CME). It has been shown[11] that CME decomposes homogeneously at 453–523°K in the gas phase to yield MVE and HCl. These products recombine instantly at room temperature to yield CME quantitatively. The first-order rate constant is given by

$$\log (k/\text{sec}^{-1}) = 11.46 - 33.3/\theta$$

where $\theta = 2.303RT$ in kcal/mole.

We examined the equilibrium established as MVE and HCl combine to form CME between 434 and 508°K. The reaction was monitored by pressure decrease, dead-space corrections being applied as necessary. The results are listed in Table II. Only the extremes of the van't Hoff plot were established, since linearity could be assumed over this range from the work on α-chloroethyl ethyl ether (CEE).[12] Since we expect the principle of group additivity[2] to hold well for ethers, our equilibrium constant should be the same as that for α-chloroethyl ethyl ether (CEE).[12]

$$\text{CME} \overset{\alpha}{\rightleftarrows} \text{HCl} + \text{methyl vinyl ether}$$

$$\text{CEE} \overset{\beta}{\rightleftarrows} \text{HCl} + \text{ethyl vinyl ether}$$

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(5) S. W. Benson, F. R. Cruickshank, and R. Shaw, *Intern. J. Chem Kinetics*, 1, 29 (1968).

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

(7) N. L. Owen and N. Sheppard, *Trans. Faraday Soc.*, 60, 634 (1964).

(8) P. Cahill, L. P. Gold, and N. L. Owen, *J. Chem. Phys.*, 48, 1620 (1968).

(9) G. J. Janz, "Thermodynamic Properties of Organic Compounds," Academic Press, New York, N. Y., 1967, p 30.

(10) K. S. Pitzer, *J. Chem. Phys.*, 14, 239 (1946).

(11) P. T. Thomas, *J. Chem. Soc.*, 136 (1961).

(12) R. L. Failes and V. R. Stimson, *Australian J. Chem.*, 20, 1553 (1967).

Table II

MVE_I,[a] torr	HCl_I, torr	$-\Delta P$, torr	10^2K_α, atm	Temp, °K
213	227.8	49.3	77.8	507.6
94.8	106.9	52.0	4.56	433.6
112.3	111.1	65.0	4.42	434.0
141.3	185.5	99.7	4.72	433.9
64.6	106.0	8.39	86.0	507.0
28.57	104.5	3.6	92.0	508.0

[a] Methyl vinyl ether initial pressure.

We find

$$\log(K_\alpha/\text{atm}) = (34.0 \pm 1.5)/2.303R - \frac{17.5 \pm 0.7}{\theta}$$

the errors quoted, as elsewhere in this paper, being 95% confidence limits, and the mean temperature 470°K.

$$\log(K_\beta/\text{atm}) = \frac{31.1 \pm 0.9}{2.303R} - \frac{16.5 \pm 0.5}{\theta}$$

Examination of the van't Hoff plot (Figure 1) reveals that the quality of the data in both cases is such that a common value of $\Delta H \sim 17.0$ kcal/mole fits both curves, whence $\Delta S_\alpha = 32.7$ gibbs/mole and $\Delta S_\beta = 32.3$ gibbs/mole. If the stable form of these ethers has the Cl atom *cis* to the methyl group, this difference in ΔS, although small, is not unexpected, an even larger "*cis* effect" being found in but-2-ene.[2]

We estimate $\overline{\Delta C_p{}^\circ{}_\alpha} \approx 0 \pm 1$ gibbs/mole, so that $\Delta S_\alpha{}^\circ{}_{298} = 32.7$ gibbs/mole, and $S^\circ{}_{298}$(CME) = 82.4 gibbs/mole. Now $S^\circ{}_{298}$(2-chlorobutane) = 84.9 gibbs/mole, taking account of optical isomerism, so that the isoelectronic replacement rule gives too low a value for $S^\circ{}_{298}$(CME) by about 2.5–0.6 = 1.9 gibbs/mole. This implies some rotational inhibition in the chloro ether, which is compatible with its observed extra stability and probable preference for a *cis* structure.

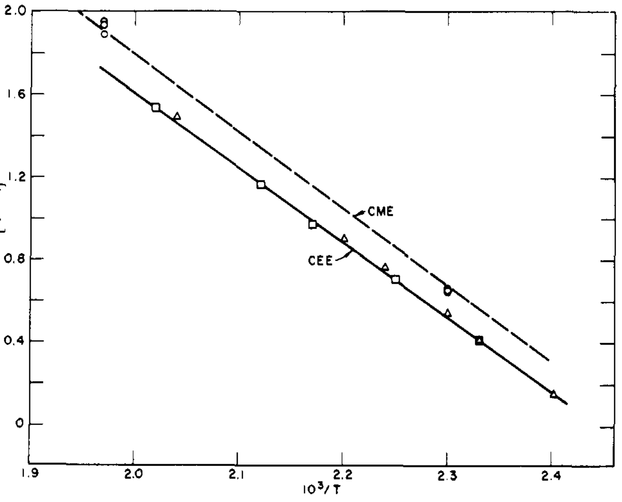

Figure 1. van't Hoff plot: (△) from combination and (□) decomposition (ref 12) and (○) present work. Solid line corresponds to van't Hoff parameters given in the text for initial data. Dashed line corresponds to common value of the heat of reaction of 17.0 kcal/mole and is the one adopted for calculation.

As in the case of CEE[12] the bimolecular combination rate constant for HCl and MVE was irreproducible and clearly surface dependent, so that K_α could not be calculated from the individual rate constants. Again, since estimates of $\overline{\Delta C_p{}^\circ{}_\alpha} \sim 0 \pm 1$ gibbs/mole, $\Delta H_f{}^\circ{}_{298}$(CME) = -65.20 ± 1.2 kcal/mole, $\Delta H_f{}^\circ$(MVE) = -26.2 kcal/mole, having been estimated by group additivity.[2]

$\Delta H_f{}^\circ{}_{298}$(CME) can be estimated in a number of ways. One method is based on the rule of additivity of bond energies[13] and leads to a value of -55.5 kcal/mole. A second method, and generally more reliable, is based on atom substitution changes. It is known that the replacement of an H atom, from a secondary position in a hydrocarbon by a Cl atom, leads to a decrease in $\Delta H_f{}^\circ$ of 7.8 kcal/mole. Applying this rule to $\Delta H_f{}^\circ(CH_3OCH_2CH_3)$ = -51.6 kcal/mole leads to an estimated $\Delta H_f{}^\circ$(CME) = -59.1 kcal/mole in reasonable agreement with the bond additivity estimate. (This value, -59.1, includes a 0.3-kcal of oxygen *gauche* correction.[2])

In either case, we notice that the observed value of -65.2 kcal/mole is more stable by from 6.1 to 9.7 kcal/mole, indicating an appreciable interaction of the Cl and O atoms across the saturated CH group. This is typical of such interactions[14] and is consistent with the low entropy of the CME compared to isoelectronic replacement rule estimates.

Iodomethyl Methyl Ether. The mechanism already proposed[5] for the reaction of dimethyl ether (DME) with iodine is

$$I_2 \rightleftarrows 2I\cdot \qquad K_{I_2}$$

$$I\cdot + \text{DME} \underset{-1}{\overset{1}{\rightleftarrows}} \text{HI} + CH_3OCH_2\cdot\ (\text{E}\cdot)$$

$$\text{E}\cdot + I_2 \underset{-2}{\overset{2}{\rightleftarrows}} \text{IME} + I\cdot$$

$$\text{E}\cdot \overset{3}{\rightarrow} CH_3\cdot + CH_2O$$

$$CH_3 + I_2 \underset{-4}{\overset{4}{\rightleftarrows}} CH_3I + I\cdot$$

$$CH_3 + \text{HI} \underset{-5}{\overset{5}{\rightleftarrows}} CH_4 + I\cdot$$

$$CH_2O + I\cdot \underset{-6}{\overset{6}{\rightleftarrows}} \text{HI} + \cdot\text{CHO}$$

$$\cdot\text{CHO} + I_2 \underset{-7}{\overset{7}{\rightleftarrows}} \text{ICHO} + I\cdot$$

$$\text{ICHO} \underset{(\text{wall})}{\overset{8}{\rightarrow}} \text{HI} + \text{CO}$$

For this system it has been shown[6] that a plot of

$$\left[\left(\frac{d[I_2]}{dt}\right)\Big/\left(k_1[I\cdot]_t[\text{DME}]_t\right)\right]\left[1 + \frac{k_{-1}[\text{HI}]_t}{k_2[I_2]_t}\right]$$

(abbreviated to β in Figure 2) against K_{app} = $([\text{HI}]_t[\text{IME}]_t/[I_2]_t[\text{DME}]_t)$ should have slope $-1/K_{eq}$ and unit intercept.

$$\text{DME} + I_2 \rightleftarrows \text{IME} + \text{HI} \qquad K_{eq}$$

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(13) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(14) A similar interaction of comparable magnitude occurs in 1,3-dioxane, which is 7.6 kcal/mole more stable than 1,4-dioxane.[2]

Table III

	Initial pressures								
Run	I_2, torr	DME, torr	$[I_2]_t$, torr	$[E]_t$, torr	K_{app} × 10^4	$-(d[I_2]/dt)_t$, torr/sec	$[HI] = [IME] = \Delta[I_2]$, torr	t, sec	Temp. °K
4	16.65	109.4	14.16	106.9	41	17.23	2.49	900	556.7
8	16.90	111.1	14.60	108.8	33.3	20.1	2.3	760	556.4
10	8.97	96.1	7.0	94.1	59	6.3	1.97	1400	556.1
14	14.4	74.5	12.8	72.9	27.4	109	1.6	14	631.6
			11.2	71.3	128	178	3.2	44	
15	12.38	64.02	11.05	62.69	25.4	109	1.33	15	631.6
			9.75	61.4	116	238	2.63	40	
16	10.49	54.2	9.33	53.04	27.0	65	1.16	15	631.6
			8.20	51.9	123	131	2.29	50	
17	8.92	46.08	8.24	45.4	123	59.8	0.68	15	631.6
			7.1	44.26	105	136	1.82	50	
18	7.68	39.62	7.06	39.0	13.9	47.1	0.62	16	631.6
			6.0	37.94	124	115	1.68	61	
19	16.1	179.3	14.02	178.2	17.4	2.32	2.08	6126	516.9
20	16.35	552.5	12.62	548.8	20.1	5.07	3.73	5313	515.1
21	3.76	584.8	3.00	584	3.29	4.07	0.76	1748	515.1
22	18.85	592.3	16.96	590.4	3.54	8.12	1.89	2128	515.3

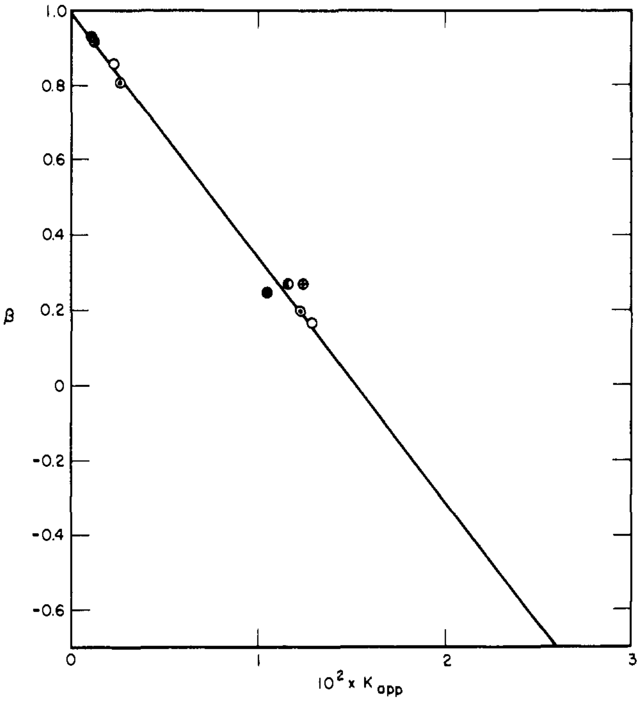

Figure 2. Typical plot of β *vs.* K_{app} for runs at 631.6°K.

Since the ordinate is unity when the abscissa is zero, the accuracy of determination of the slope of the linear plot is greatly improved by constraining the line to pass through this theoretical point.

Data for the runs used are listed in Table III and Figure 2 shows a typical plot of β against K_{app} for runs at 631.6°K, incorporating data for the initial and late stages of each run. At this temperature some cleavage of the E· radicals occurs,[6] becoming significant in the latter stages of reaction. For this reason, the actual equilibrium is never set up and must be deduced from the above relation. The cleavage is insignificant about the center of the temperature range when equilibrium can be set up and approached from both sides.

Table IV

DME, torr	I_2, torr	IME, torr	HI, torr	Temp, °K	K_{eq} × 10^2
471	11.85	3.0	21	553.3	<1.13
105	12.4	4.0	4.0	556.7	>1.23
216.7	15.05	1.64	17.7	552.0	<1.03

Table V

10^2K_{eq}	Temp, °K	θ
1.00	515	2.35
1.09	556	2.55
1.51	631.6	2.89

In these experiments, HI was added to the I_2–DME mixture until $d[I_2]/dt$ changed sign, thus establishing bounds to the equilibrium constant. It was experimentally difficult to get the upper and lower limits closer than about 10% of each other, since HI, unlike HCl, dissolves rapidly in the silicone stopcock grease of the several stopcocks outside the reaction vessel. Dead-space corrections were reduced by flushing the dead space with argon after the HI addition. The error in K_{eq}, so determined, is about ±15%, and the results appear in Table IV.

At the lowest temperatures, HI reacts slowly with DME, presumably on the surface by analogy with tetrahydrofuran and HI,[15] so that the above relation must again be used.

The values of K_{eq} calculated from the above reaction are listed in Table V and are shown in van't Hoff form in Figure 3, in which the best line drawn by inspection is represented by

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[15] S. W. Benson and F. R. Cruickshank, *J. Am. Chem. Soc.*, in press.

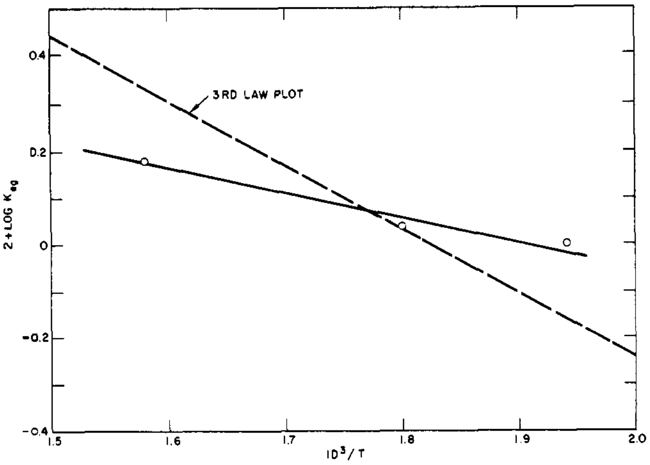

Figure 3. van't Hoff plot from values of K_{eq} in Table V.

$$\log K_{eq} = -\frac{4.46 \pm 1.3}{4.576} - \frac{2.47 \pm 0.3}{\theta}$$

In view of the relatively close agreement between the two methods of evaluating K_{eq} at 556°K and the linearity of Figure 2, the above results should be reasonably accurate. Should the linearity of Figure 2 be fortuitous, however, in view of the unexplained[6] iodine-producing reaction and the correction for radical cleavage, K_{eq} may have a rather higher value at 631°K than we observed. Similarly, surface reactions complicate the rate expression at the lowest temperatures.

The van't Hoff plot in Figure 3 yields $\Delta H = 2.47 \pm 0.3$ kcal/mole and $\Delta S = -4.46 \pm 1.3$ gibbs/mole at a mean temperature of 570°K. We can estimate the ΔC_p of this reaction to have a mean value of 1.4 ± 1 gibbs/mole over the interval 300–600°K. This value yields $\Delta H_{298} = 2.1$ kcal/mole and $\Delta S_{298} = -5.5$ gibbs/mole. Combining these with the known data[16] on I_2, HI, and $(CH_3)_2O$, we find that $S°_{298}$(IME) = 70.9 gibbs/mole and $\Delta H_f°_{298} = -33.3$ kcal/mole.

If we compare $S°_{298}$(IME) with the isoelectronic *n*-propyl iodide for which $S°_{298}$(*n*-propyl iodide) = 80.1 gibbs/mole,[17,18] we see an unexpectedly large discrepancy of 9.2 gibbs/mole. This is an impossibly high difference which cannot be ascribed to a high rotational barrier. Even a large increase in the barrier to rotation around the ICH_2–OCH_3 bond of 10 kcal would not account for a loss of more than about 1.5 gibbs/mole. It would, in fact, require the formation of a tight four-membered ring to have an entropy as low as 70.9 gibbs/mole at 298°K. For example, the entropy of trimethylene sulfide is 68.1 gibbs/mole.[2] If we correct its translational entropy to the same molecular weight as IME, we obtain a value of 70.6 gibbs/mole. Further correction of the rotational entropy for the mass difference would increase this to about 72.6. By comparison, the measured value of $S°$(IME) is unacceptably low.

Accordingly, particularly in view of the experimental uncertainties at the extremes of the van't Hoff plot, we feel justified in assigning an entropy to IME by the replacement rule method and calculating $\Delta H_f°$ on the basis of our mean temperature equilibrium constant being accurate.

Based on the difference between $S°_{298}$(CME) = 82.4 gibbs/mole and the IRR value for 2-chlorobutane of 84.9, we shall assign an entropy difference of 2.5 ± 1 gibbs/mole between IME and *n*-PrI. This then yields a value of $S°_{298}$(IME) = 77.6 ± 1 gibbs/mole. This is 6.7 gibbs/mole higher than the value deduced from the van't Hoff plot (Figure 3) and suggests that ΔS for the iodination of Me_2O at a mean temperature of 570°K should similarly be raised by 6.7 gibbs/mole to a value of $\Delta S_{570} = 2.2$ gibbs/mole. This value of the entropy, together with the most reliable measured value of the K_{eq}, namely that at 556°K (Table V), yields $\Delta H°_{556} = 6.2$ kcal/mole or 3.7 kcal/mole higher than the van't Hoff value. Figure 3 shows the van't Hoff plot obtained, using these values for ΔH and ΔS. It suggests systematic errors in the measured values of K_{eq} at the extreme temperature of 50%. While these are three times larger than our precision, they are not unreasonably large relative to the difficulties of the measurement. However, they represent errors in $\Delta G°$ for the reaction of only 0.4 kcal/mole.

The above value of $\Delta H°_{556}$, together with the estimated $\langle \Delta C_p° \rangle$ for the reaction, yields $\Delta H_f°_{298}$(IME) = -29.3 kcal/mole. From bond additivity rules[13] we obtain a value very close to this, namely, -29.1 kcal/mole, while from the atom substitution rule, based on hydrocarbons, we estimate a value of -26.0 kcal/mole. In both cases, we see that the measured value of $\Delta H_f°$(IME) is only slightly more stable than the estimated value, indicating a much weaker interaction of the I and O atoms than in the case of O and Cl, or two O atoms linked to a saturated C atom. If the interaction is polar in character, then the effect would be expected to be less in the iodo ether than in the chloro ether. Presumably, the carbon atom attached to the oxygen atom acquires a partial positive charge, and this results in an increased attraction for the substituted halogen atom on the opposite carbon atom, which bears a partial negative charge. If we simply calculate the coulombic interaction between the Cl atom and the end C atom in Cl–CH_2OCH_3 in the *gauche* conformation (C–Cl distance = 3.0 Å) with 0.23 partial electronic charge localized at the Cl and C atoms, we estimate an attractive energy of about 5.8 kcal.[19] For the I atom with only 0.16 partial charge, and a C···I distance of 3.3 Å, we calculate a 3.7-kcal interaction in reasonable semiquantitative accord with the observations.

Similar values are obtained if we estimate dipole–dipole interactions between the O–C dipole in the ether and the C–Cl or C–I dipoles. It may be argued that the interactions are constituted by either a nonbonded, π-electron attraction across space, or by hyperconjugation across the saturated C atom. If either of these explanations were correct, we should expect to see similar enhancements in stability in the series CH_4, CH_3X, CH_2X_2, CHX_3, CX_4, where X is an atom with lone pairs.

The heats of formation in the chlorine, bromine, and

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(16) D. P. Stull, Ed., "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1963.

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(19) The partial changes are calculated from the dipole moments in Me_2O, MeI, and MeCl, by dividing the dipoles by the appropriate bond lengths. Data on lengths from "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, and dipole moment data from A. L. McClellan, "Tables of Experimental Dipoles," W. H. Freeman and Co., San Francisco, Calif., 1963.

iodine series show on the contrary[2,20] an actual destabilizing effect of increased halogen substitution. Thus in the chlorine series, we have $\Delta H_f°(CH_4) = -17.8$, $\Delta H_f°(CH_3Cl) = -20.7$, $\Delta H_f°(CH_2Cl_2) = -22.4$, $\Delta H_f°(CHCl_3) = -25$, and $\Delta H_f°(CCl_4) = -26.0$, all in kcal/mole.

It appears from this that the data presented here are compatible with a nonbonded electrostatic interaction arising from alternate polarity of atoms in *gauche* conformations. If this is correct, we should expect to see similar interactions in other related compounds. For example, 1,3-dichloro, or difluoro, or dicyano compounds might be expected to show a preference for *gauche* conformations with the negative halogen near the positive carbon. Effects in these compounds will not be as great as with the present types because of the compensating effects of increased halogen–halogen repulsion in the *gauche* conformations.

From our results we can calculate $\Delta H_f°$ and $S°$ contributions for the following groups.[2]

	$\Delta H_f°$, kcal/mole	$S°_{298}$, gibbs/mole
C–(H$_2$)(O)(I)	+3.8	40.7[a]
C–(H)(C)(O)(Cl)	−22.3	15.9

[a] Value assigned.

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Ligand-Exchange Kinetics and Solution Equilibria of Cadmium, Zinc, and Lead Nitrilotriacetate Complexes[1a-c]

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Abstract: Proton nuclear magnetic resonance (nmr) techniques have been used to study the aqueous solution chemistry of the nitrilotriacetate (NTA) complexes of cadmium, zinc, and lead. Complexes having NTA-to-metal ratios of 1 and 2 are present, depending upon the solution conditions, and their formation constants were evaluated from chemical shift data. The kinetics of ligand exchange between the free and the complexed forms were measured using nmr line-broadening techniques. Exchange was found to occur by both first-order dissociation of the metal–ligand complexes and by second-order processes involving free ligand and metal–ligand complexes. The rate constants for each of the reactions resulting in ligand exchange were evaluated from the dependence of the exchange rate upon ligand concentration and pH. It was observed that, when the free NTA is in the monoprotonated form, the rate of ligand exchange is significantly less than the rate when the NTA is in the totally ionized form. From comparisons of the rate constants in these and in other systems, mechanisms to explain the dependence of the exchange rate on the degree of protonation of the reacting ligand are discussed. It is proposed that the decrease in rate is due to the relatively slow rate of proton migration from the nitrogen atom in a partially bonded reaction intermediate. Possible structures for the NTA complexes are discussed based on the kinetic rate constants, the equilibrium formation constants, and the heteronuclear coupling observed in the nmr spectra for several of the complexes.

In earlier papers, proton nuclear magnetic resonance (nmr) line-broadening studies of the ligand-exchange kinetics in the strontium–ethylenediaminetetraacetic acid (EDTA) and calcium–EDTA systems were reported.[2,3] The rate of EDTA exchange between the free and complexed forms was measured, and the reactions resulting in exchange were established. In those systems, exchange occurs by first-order dissociation of the metal–EDTA complex and by second-order processes involving direct reaction of the free EDTA with the metal–EDTA complex. From the measured dissociation rate constants and the appropriate equilibrium constants, rate constants were calculated for the formation of the metal–EDTA complexes by reaction of the aquated metal ion with the EDTA tetraanion (eq 1) and with monoprotonated EDTA (eq 2). Rate constants calculated for reaction 1 are

$$M^{2+} + EDTA^{4-} \rightarrow M(EDTA)^{2-} \tag{1}$$

$$M^{2+} + HEDTA^{3-} \rightarrow M(EDTA)^{2-} + H^+ \tag{2}$$

approximately those predicted for a mechanism in which water loss from the aquated metal ion is rate determining. However, the rate constants calculated for reaction 2 are from two to three orders of magnitude smaller than predicted for a similar rate-determining mechanism. This is in contrast to the reactions of Ni(II), Co(II), Cu(II), Zn(II), and Cd(II) with $HEDTA^{3-}$ to form the corresponding $M(EDTA)^{2-}$ complexes.[4-8] For the latter reactions, the observed rate constants all agree with the

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