This implies there is a mixing of the wave functions from structures a and c in the ester radical, in preference to structures a and b, which leaves the relative stability of the radical unchanged.

Previous discussion has been confined to discussion of the stabilization energy with respect to a hydrogen atom. For consideration of resonance energies arising from electron delocalization, it is more appropriate to compare the rate with respect to the corresponding alkyl substituent. In alkanes, C–H bond strengths show a uniform decrease of 98, 95, and 92 kcal/mol for the formation of primary, secondary, and tertiary radicals.[2b] Similarly, C–C bond strengths in ethane, propane, and butane (2–3 bond) show the same uniform decrease of 88, 85, and 82 kcal/mol, respectively.[2b] Alkyl substitution in the position β to the breaking bond does not affect the bond strength, the 1–2 bond strength of butane being 85 kcal/mol. To a good approximation, substitution of a hydrogen atom by a carbon atom decreases the α-bond strength by 3 kcal/mol.

On this basis, the radical resonance energy of the α-carbomethoxy group is only 1.0 kcal/mol. This is not unreasonable compared with a similarly defined resonance energy of 2.7 kcal/mol in the methylacetonyl radical.[5] The difference is due to the effect of structure c in reducing the additional electron delocalization.

Conclusion

The radical stabilization energy of an α-carbomethoxy group has been shown to be 4.0 ± 1.7 kcal/mol as derived from the solution kinetics for the isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane with respect to a hydrogen atom; a calculation based upon the reported isomerization of 1,4-dicarbomethoxybicyclo[2.2.0]hexane yields an identical value of 4.0 ± 1.9 kcal/mol. The excellent agreement between these values is strong support for the accuracy of the reported rates of isomerization of bicyclo[2.2.0]hexane, 1,4-dichlorobicyclo[2.2.0]hexane, 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane, and 1,4-dicarbomethoxybicyclo[2.2.0]hexane, which were measured in five independent laboratories, and the assumptions of the biradical mechanism used in the derivation of the stabilization energies. Furthermore, the relative magnitude of the stabilization energy compared with 5.7 ± 1.7 kcal/mol in the methylacetonyl radical[5] is in good agreement with known differences in the bonding of esters and ketones. It should be noted that this stabilization energy in the methylacetonyl radical was derived from the rate of reaction between iodine and methyl ethyl ketone and incorporates none of the assumptions of the biradical mechanism.

Conformational Analysis. II. The Molecular Structure, Composition, and Trans–Gauche Energy and Entropy Differences and Potential Hindering Internal Rotation of Gaseous Oxalyl Bromide as Determined by Electron Diffraction[1]

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Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received January 29, 1973*

Abstract: Gaseous oxalyl bromide has been studied by electron diffraction at nozzle temperatures of 6, 80, and 211°. As in the case of oxalyl chloride, reported earlier, the molecules exist as a mixture of trans and gauche conformers instead of trans and cis as had been previously supposed. The "bent" single bond pair concept of the double bond accounts nicely for the instability of the cis form relative to the gauche. Assuming that the conformers differ only in their torsion-angle values, the values of some of the more important parameters at 6° with estimated errors of 2σ are $r_{\mathrm{C=O}} = 1.177$ (0.003) Å, $r_{\mathrm{C-C}} = 1.546$ (0.008) Å, $r_{\mathrm{C-Br}} = 1.925$ (0.004) Å, $\angle\mathrm{CCO} = 124.6$ (0.5)°, $\angle\mathrm{CCBr} = 111.6$ (0.5)°, ϕ (the gauche torsion angle relative to 0° for the trans form) = 114.1 (19.9)°, $l_{\mathrm{C=O}} = 0.0337$ (0.0053) Å, $l_{\mathrm{C-C}} = 0.0450$ Å (assumed), $l_{\mathrm{C-Br}} = 0.0480$ (0.0069) Å, and δ (the rms torsion amplitude for the trans conformer) = 30.7 (7.6)°. The mole fractions of the trans conformer at 6, 80, and 211° are 0.480 (0.095), 0.423 (0.099), and 0.359 (0.124), respectively, from which the energy difference ($\Delta E^\circ = E^\circ_{\mathrm{g}} - E^\circ_{\mathrm{t}}$) and the entropy difference ($\Delta S^\circ = S^\circ_{\mathrm{g}} - S^\circ_{\mathrm{t}}$) are calculated to be 0.63 kcal/mol ($\sigma = 0.32$) and 1.1 cal deg^{-1} mol^{-1} (0.9). The experimental results allow the determination of the rotational potential function assumed to be of the form $2V = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)$; the values of the coefficients are $V_1 = 0.62 \pm 0.27$, $V_2 = 0.20 \pm 0.19$, and $V_3 = 0.43 \pm 0.21$, all in kcal/mol. The heights of the barriers separating the trans from the gauche and the gauche from the gauche forms are 0.78 ± 0.43 and 0.48 ± 0.31 kcal/mol, respectively. The predicted value for the torsional frequency of the trans form is 35 cm^{-1}, which is in good agreement with the observed 40 cm^{-1}.

In a recent article[1] we reported the results of an electron-diffraction investigation of oxalyl chloride vapor. Among these results was the mildly surprising discovery that the vapor consists of substantial amounts of a gauche ($\phi \approx 125°$) conformer instead of the s-cis ($\phi = 180°$) in equilibrium with the s-trans ($\phi = 0°$) form; interpretations of spectroscopic data,[2] which on

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(1) For paper I of this series see K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 1003 (1973).

(2) See ref 1 for a summary.

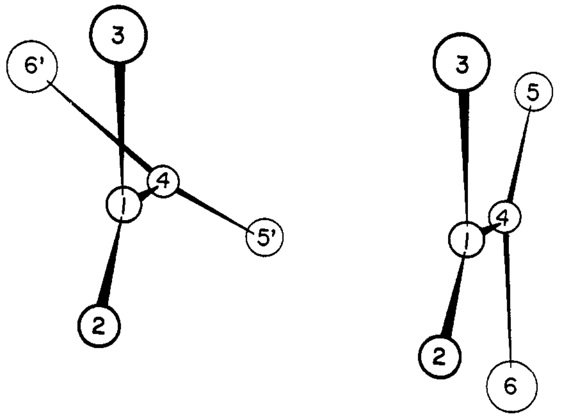

Figure 1. Diagrams of the gauche and trans forms of oxalyl bromide with atom numbering.

balance had favored the presence of two conformers in the gas and liquid phases, had always been expressed in terms of a mixture of the cis and trans forms.

Oxalyl bromide has been less extensively studied than the chloride, but the structural conclusions have been similar. The molecules are certainly trans in the crystal.[3–5] However, spectroscopic studies of the fluid phases have led both to the conclusion that only the trans conformer is present[5,6] and that two conformers (taken, as in oxalyl chloride, to be cis and trans) are present.[4] Our electron-diffraction investigation of oxalyl bromide vapor shows that there are indeed two conformers present in major proportion and that, as in oxalyl chloride, they are the gauche and trans forms (Figure 1).

Experimental Section

Materials. Oxalyl bromide (>95%) from the Aldrich Chemical Co. was used without further purification. Before each diffraction experiment, however, the sample bulb was pumped for brief periods.

Apparatus and Data Reduction. The experiments were carried out at nozzle-tip temperatures of 6, 80, and 211° under conditions very similar to those described for oxalyl chloride.[1] However, instead of drawing background curves by hand, these curves were calculated with a new computer program[7] which has greatly simplified this task and which is now in general use in this laboratory. Each of the composite experimental intensity curves (Figure 2) contains data from four plates made at the long and four at the intermediate nozzle-to-plate distance.[8]

Structure Analysis[9]

Radial Distribution Curves. The experimental radial distribution curves are shown in Figure 3. The origins of the various peaks of these curves may be deduced by referring to Figure 1 and to the labeled vertical lines on the 211° theoretical curve.

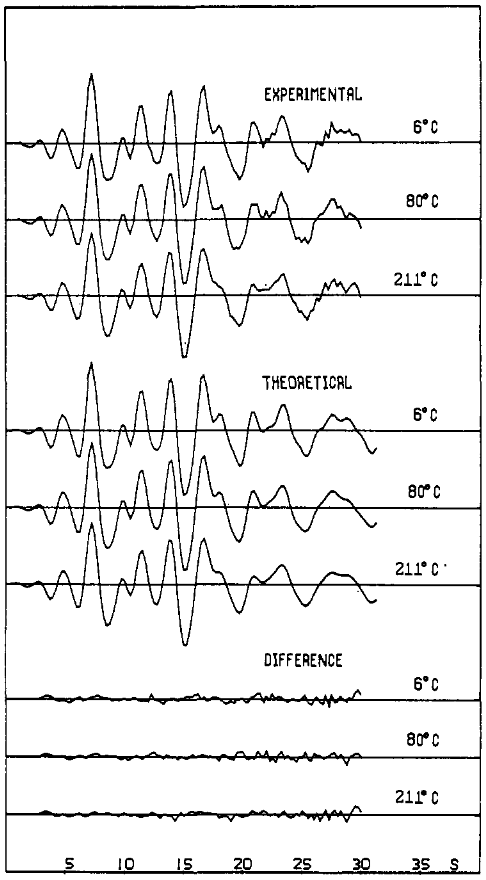

Figure 2. Intensity curves for oxalyl bromide. The experimental curves are composites of data from several experiments; the theoretical curves were calculated from the parameter values of Table I. All curves are on the same scale and are in the form $sI_m(s)$ (see ref 1).

That the gaseous samples comprise more than one conformer is clearly revealed by the temperature dependence of the last peak in the radial distribution curves. This peak arises from the Br···Br distance in the trans conformer; the variation of peak area with temperature corresponds to a variation in the fraction of trans present. The identity of the other conformer(s) is not immediately obvious from the appearance of the rotation-sensitive part of the radial distribution curves ($r > 3.0$ Å). However, as in oxalyl chloride it was found that combinations of the trans ($\phi = 0°$) and gauche ($\phi \approx 125°$) forms having the same structure (except for the torsion angle) gave theoretical curves in good agreement with observation whereas all combinations of the cis and trans forms gave very poor agreement.

Structure Refinement. As in the case of oxalyl chloride, the least-squares refinements were carried out in terms of a model described by a composition parameter, six geometrical parameters ($r_{C=O}$; r_{C-C}; r_{C-Br}; $\angle CCO$; $\angle CCBr$; and ϕ_g, the torsion angle of the gauche form), and nine amplitude parameters ($l_{C=O}$; l_{C-Br}; l_{C-C}; l_{15}; $l_{23} = l_{16}$; l_{26}; l_{36}; $l_{36'} = l_{25'} = l_{26'}$; and δ, the root-mean-square amplitude of the torsional oscillation of the trans form). "Shrinkage" corrections[10] of about 0.01–0.02 Å were applied to the O···O,

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(3) P. Groth and O. Hassel, *Acta Chem. Scand.*, **16**, 2311 (1962).

(4) J. R. Durig, S. E. Hannum, and F. G. Baglin, *J. Chem. Phys.*, **54**, 2367 (1971).

(5) H. Shimada, R. Shimada, and Y. Kanda, *Bull. Chem. Soc. Jap.*, **41**, 1289 (1968).

(6) K. G. Kidd and G. W. King, *J. Mol. Spectrosc.*, **28**, 411 (1968).

(7) L. Hedberg, to be published.

(8) For each temperature the least-squares refinements of the structure were based upon a simultaneous adjustment to two curves, a composite of the data from the long and one from the short nozzle-to-plate distances, rather than on the individual component curves as was done in the case of oxalyl chloride. The data for these composite curves will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4796. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(9) A description of the details of the structure analysis is omitted since they are essentially identical with those given in ref 1 and in references cited therein.

(10) O. Bastiansen and M. Traetteberg, *Acta Crystallogr.*, **13**, 1108 (1960).

Table I. Final Structural Results[a,b] for Oxalyl Bromide at Different Temperatures

Parameter[c]	6° r_a	6° l^d	80° r_a	80° l^d	211° r_a	211° l^d
C=O	1.177 (0.003)	0.0337 (0.0053)	1.182 (0.003)	0.0328 (0.0056)	1.176 (0.003)	0.0370 (0.0049)
C—C	1.546 (0.008)	[0.0450]	1.539 (0.008)	0.0463 (0.0142)	1.536 (0.008)	[0.0480]
C—Br	1.925 (0.004)	0.0480 (0.0069)	1.925 (0.004)	0.0490 (0.0066)	1.930 (0.004)	0.0561 (0.0065)
$C_1\cdots O_5$	2.416 (0.008)	0.0534 (0.0092)	2.419 (0.010)	0.0650 (0.0097)	2.409 (0.010)	0.0624 (0.0097)
$C_1\cdots Br_6$	2.879 (0.008)	0.0509 } (0.0090)	2.874 (0.010)	0.0582 } (0.0090)	2.875 (0.015)	0.0676 } (0.0107)
$O_2\cdots Br_3$	2.759 (0.005)	0.0509 }	2.759 (0.005)	0.0582 }	2.760 (0.006)	0.0676 }
$O_2\cdots Br_6$	3.102 (0.025)	0.0645 (0.0131)	3.109 (0.032)	0.0786 (0.0296)	3.122 (0.080)	0.0738 (0.0419)
$O_2\cdots O_5$	3.439 (0.022)	[0.0600]	3.448 (0.019)	[0.0600]	3.419 (0.034)	[0.0600]
$Br_3\cdots Br_6$	4.562 (0.034)	0.0690 (0.0255)	4.553 (0.032)	0.0729 (0.0159)	4.532 (0.086)	0.0821 (0.0240)
$O_2\cdots Br_{6'}$	3.755 (0.147)	0.2905 }	3.773 (0.141)	0.3126 }	3.459 (0.094)	0.2931 }
$O_2\cdots O_{5'}$	3.068 (0.099)	0.2905 } (0.1350)	3.070 (0.097)	0.3126 } (0.1278)	3.035 (0.065)	0.2931 } (0.1090)
$Br_3\cdots Br_{6'}$	3.545 (0.285)	0.2905 }	3.509 (0.278)	0.3126 }	3.793 (0.194)	0.2931 }
∠CCO	124.6 (0.5)		125.0 (0.5)		124.8 (0.7)	
∠CCBr	111.6 (0.5)		111.6 (0.5)		111.6 (0.8)	
ϕ^e	114.1 (19.9)		116.3 (19.6)		120.0 (13.5)	
δ^f	30.7 (7.6)		24.7 (7.9)		35.8 (14.3)	
% trans	48.0 (9.5)		42.3 (9.9)		35.9 (12.4)	
R^g	11.2		11.1		11.4	

[a] Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. [b] Parenthesized values are 2σ and include estimates of systematic error. See V. Plato and K. Hedberg, *Inorg. Chem.*, **10**, 590 (1971). [c] Unprimed items refer either to non-torsion-sensitive distances or to torsion-sensitive distances in the trans conformer. Primed items refer to torsion-sensitive distances in the gauche conformer. Torsion-sensitive distances in the trans conformer are $r_g(1)$ values (weighted averages of the nine different representations of each distance; see ref 1). [d] Quantities in braces were refined with constant differences as a group; quantities in brackets were assumed. [e] The average torsion angle in the gauche form relative to 0° for the trans conformation. [f] The root-mean-square amplitude of the torsional motion in the trans conformer. [g] $R = [\Sigma w_i\Delta_i^2/\Sigma w_i I_i^2(\text{obsd})]^{1/2}$ where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$.

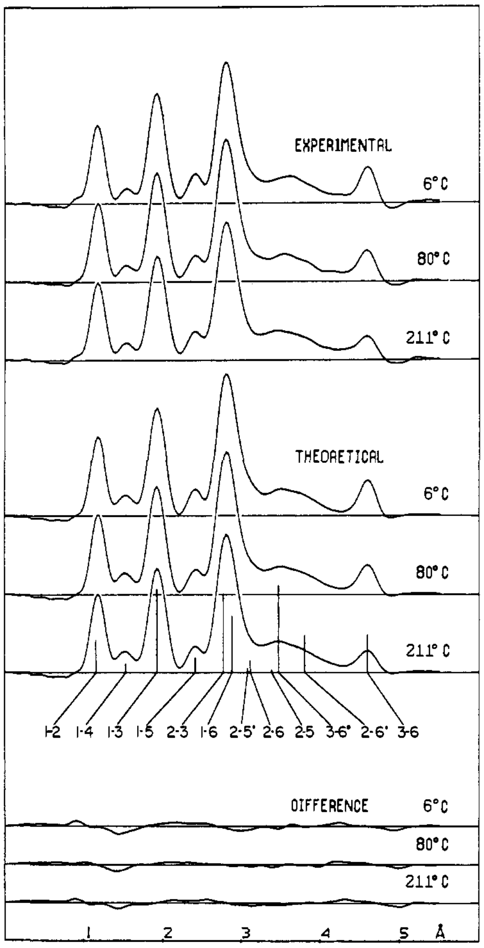


Figure 3. Radial distribution curves for oxalyl bromide. The curves were calculated from the intensity curves of Figure 1 with $B = 0.0025$. Unobserved experimental intensity data for the region $0 < s < 1.75$ were taken from the theoretical curves. The vertical lines indicate the interatomic distances in the final models; the lengths of the lines are proportional to the weights of the distances. All curves are on the same scale.

O···Br, and Br···Br distances in the trans form. This description of the system implies that the structures of the two forms are identical except for the torsion angles. The final results are given in Table I, and the theoretical intensity and radial distribution curves corresponding to them are shown in Figures 2 and 3 together with difference curves. The correlation matrix for the 6° result is given in Table II; the other two correlation matrices are similar and will appear in the microfilm edition of this journal.

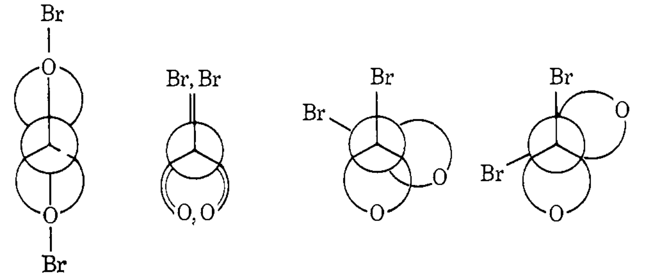
Discussion

Molecular Structures and Bonding. The values of the distances and angles in Table I show no significant variation with temperature while, as expected, the amplitudes tend to increase with increasing temperature. The good consistency of the values of the individual distances and angles (every pair is encompassed by the sum of their associated errors) suggests that any of the sets of results adequately describes the structure of both gauche and trans oxalyl bromide. Since, contrary to assumption, the non-torsion-sensitive distances and angles cannot be identical in these two forms, the results of Table I are really averages. However, because the amplitudes associated with these distances have magnitudes about as expected for a single conformer, it seems clear that the geometries of the gauche and trans forms aside from the torsion angle must be nearly the same.

The bond angles in oxalyl bromide are very nearly the same as in oxalyl chloride (∠CCO = 124.2 ± 0.3°, ∠CCCl = 111.8 ± 0.2°). The carbon–oxygen distance is slightly shorter and the carbon–carbon distance and slightly longer (oxalyl chloride: $r_{C=O} = 1.181 \pm 0.002$ Å, $r_{C-C} = 1.528 \pm 0.005$ Å) in the bromide, in agreement with the smaller degree of conjugation presumed to operate in this compound.

Although the R values for the oxalyl bromide refinements are as good as those for oxalyl chloride, comparison of the radial distribution difference curves suggests the possibility that the structure determination is a bit better for the latter. We investigated the possibility that an unrecognized small amount of the cis conformer in the oxalyl bromide sample might account for the slightly poorer difference curves. The inclusion of cis conformer in amounts greater than ~10% significantly worsened both the appearance of the difference curves and the values of R. We have no evidence for the presence of a cis conformer in any amount in our samples. A question that remains concerns the adequacy of the trans–gauche model itself. The measured torsional amplitude (~30) of the trans model is large and that of the gauche form, treated in the refinements only as an apparent augmentation of the effect of frame vibrations, could well be even larger. One might expect that, depending on the form of the rotational potential function, a substantial fraction of the sample molecules could have conformations intermediate between trans and gauche. As will be seen in a later section, the energy difference between the trans and gauche forms and the barrier separating the gauche from the trans are small enough to lend substance to this notion.

In oxalyl chloride the presence of the gauche conformer instead of the cis in equilibrium with trans was suggested to be the consequence of a balance among the energies of conjugation (E_C), peripheral-atom repulsion ($E_A = E_A(\mathrm{Cl}\cdots\mathrm{Cl}) + E_A(\mathrm{O}\cdots\mathrm{O})$ and $E_A' = 2E_A'(\mathrm{Cl}\cdots\mathrm{O})$), and peripheral-bond electron pair repulsion (E_B); the latter involved the concept of a double bond as being formed from two "bent" single bonds.[11] This explanation may also be applied in an entirely analogous way to oxalyl bromide. The structures of the various forms and the relative energies deduced from them are



trans	cis	gauche	skew
$E_A' - E_C$	$E_A - E_C + E_B$	0	E_B

The relative abundances of these forms lead to the same qualitative result as in oxalyl chloride: $E_B \gg 0$, $E_C > E_A'$, and $E_B \gg E_C - E_A$.

Energy and Entropy Differences of the Conformers. The temperature dependence of the composition of the gaseous sample is given by the formula

$$\frac{N_g}{N_t} = 2e^{\Delta S°/R}e^{-\Delta E°/RT} \qquad (1)$$

where N_g and N_t are the fractions of the gauche and trans molecules and the factor 2 is the ratio of the statistical weights of the two forms. Figure 4 shows the variation of sample composition with temperature. The results with estimated standard deviations are

Table II. Correlation Matrix for Parameters of Oxalyl Bromide at 6°[a]

	r_{C-C}	$r_{C=O}$	r_{C-Br}	∠CCO	∠CCBr	ϕ	$l_{C=O}$	l_{C-Br}	l_{15}	l_{16}	l_{36}	l_{26}	$l_{36'}$	% trans
σ[b]	0.0027	0.0010	0.0012	0.18	0.16	7.04	0.0018	0.0023	0.0032	0.0032	0.0045	0.0090	0.0476	0.0337
	1.000	−0.173	−0.313	−0.181	−0.191	0.076	0.171	0.139	0.057	−0.093	−0.081	−0.153	−0.031	−0.159
		1.000	−0.141	−0.019	0.269	0.026	0.025	0.067	−0.029	0.030	−0.020	−0.036	−0.005	−0.044
			1.000	0.570	−0.306	−0.042	−0.026	0.012	−0.029	0.181	0.014	0.014	0.025	0.029
				1.000	−0.684	−0.135	0.050	0.058	−0.001	0.341	0.115	0.213	0.041	0.162
					1.000	0.077	−0.052	−0.031	0.020	−0.515	−0.036	−0.089	−0.068	−0.064
						1.000	0.075	0.087	0.029	0.032	−0.080	−0.217	0.673	−0.137
							1.000	0.410	0.204	0.305	0.049	−0.111	0.004	−0.121
								1.000	0.154	0.340	0.026	−0.146	0.002	−0.133
									1.000	0.136	0.059	−0.047	−0.006	−0.020
										1.000	−0.033	0.025	0.057	−0.166
											1.000	0.404	−0.130	0.695
												1.000	0.002	0.600
													1.000	−0.185
														1.000

[a] Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. [b] Standard deviations from least squares.

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[11] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, pp 136–142.

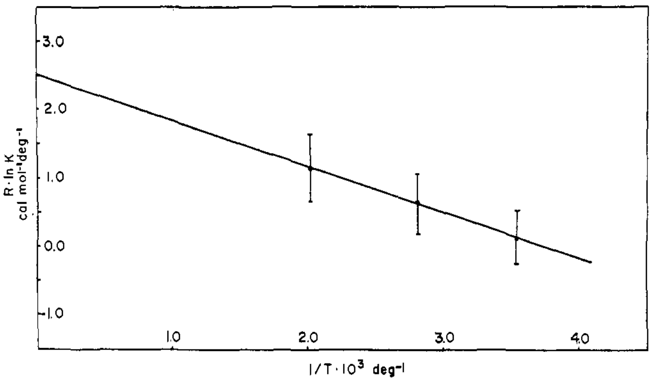

Figure 4. An Arrhenius plot of composition data. $K = N_g/N_t$. The half-lengths of the vertical bars indicate 1σ. Least squares straight line.

$\Delta E^\circ = E^\circ_g - E^\circ_t = 0.63 \pm 0.32$ kcal/mol and $\Delta S^\circ = S^\circ_g - S^\circ_t = 1.1 \pm 0.9$ cal mol^{-1} deg^{-1}. The value for ΔE° is lower than that estimated from the temperature dependence of the intensities of Raman bands measured from the liquid (2.9 ± 0.1 kcal/mol).[4] No spectroscopically derived value for the entropy difference exists. Both the energy and entropy differences of the trans and gauche conformers are smaller for oxalyl bromide than for oxalyl chloride.

Rotational Potential Function. If the hindering potential for internal rotation is assumed to be

$$2V(\phi) = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi) + \cdots \quad (2)$$

the usual power series expansion of the first three terms leads, ignoring terms larger than ϕ^2, to the harmonic approximation formula

$$V(\phi) = 0.25V^*\phi^2 \quad (3)$$

where $V^* = V_1 + 4V_2 + 9V_3$. Our electron-diffraction parameter δ is related to V^* by the formula[1]

$$V^*/(4RT) = 1/2\delta^2 \quad (4)$$

from which the values of V^* are found to be 3.9, 7.5 and 4.9 kcal/mol. The average, 5.4 ± 1.5 kcal/mol, may be taken as the best overall value. The value of V^*, the measured gauche angle of 117° (the average of the three values in Table I) which corresponds to a minimum in the potential, and the value of ΔE, which is equal to $V(\phi)$ at the gauche angle, lead to the equations

$$V_1 + 4V_2 + 9V_3 = 5.4 \text{ kcal/mol} \quad (5)$$

$$V_1 - 1.82V_2 - 0.53V_3 = 0 \quad (6)$$

$$0.727V_1 + 0.794V_2 + 0.0062V_3 = 0.63 \text{ kcal/mol} \quad (7)$$

The solutions of these equations with standard deviations estimated from the errors in V^*, ΔE, and ϕ are $V_1 = 0.62 \pm 0.27$, $V_2 = 0.20 \pm 0.19$, and $V_3 = 0.43 \pm 0.21$, all in kilocalories per mole. The potential function and its components are shown in Figure 5. The barrier separating the trans from the gauche conformer is calculated to be 0.78 ± 0.43 kcal/mol and that separating the two gauche forms to be 0.48 ± 0.31 kcal/mol.

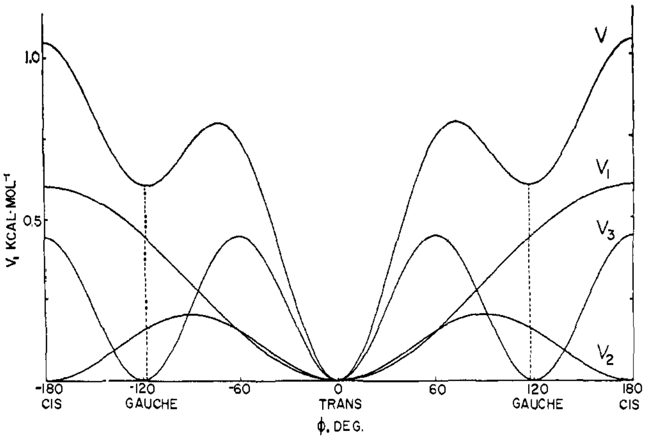

Figure 5. Form of hindering potential. The dashed lines indicate the measured gauche torsion angle.

It was mentioned in an earlier section that the form of the rotational potential might be such as to make our model of the system, *i.e.*, a system whose composition can be described in terms of conformers undergoing harmonic torsional oscillations about well-defined equilibrium torsional angles, somewhat questionable. The low barrier separating the gauche from the trans conformer (0.15 kcal/mol) supports this possibility; approximately three-fourths of the nominally gauche molecules are calculated to have thermal energies at room temperatures greater than the barrier. The practical effect of such a circumstance is a "smearing-out" of the rotation-sensitive distances for the gauche conformer. Because the barrier separating the two gauche forms is higher than that separating gauche from trans, the broadened distance distribution would at the same time be shifted toward distributions corresponding to smaller torsion angles. Thus, it may be that in the oxalyl halides the *equilibrium* gauche torsion angles are more nearly alike than is suggested by the measured, or *average*, values.

Torsional Frequencies. If it is assumed that the potential can be represented in quadratic approximation in the vicinity of the two minima, the expected torsional frequencies for the two conformers may be calculated from the formula $\nu = (2\pi)^{-1}(k/\mu_I)^{1/2}$, where $k = (d^2V/d\phi^2)_{\phi=0,117}$ and μ_I is the reduced moment of inertia. The value for the trans conformer is found to be 35 cm^{-1}, in good agreement with the observed 40-cm^{-1} frequency assigned to this mode;[4] the value calculated for the unobserved gauche torsional frequency is 13 cm^{-1}. For reasons connected with the discussion in the previous section, we regard the latter value as very uncertain.

Acknowledgment. We are grateful to the National Science Foundation which supported this work under Grant GP 27763X.