

in 10^3 collisions with the butenes and one in 10^4 collisions with ethylene. If the newly formed C_2O contains excess translational or rotational energy, then on the average this excess should be lost by collisions before reaction can occur. If vibrational relaxation of C_2O is similar to that of CO_2 or N_2O ,²⁷ then C_2O should have thermal energies before it reacts, except possibly for the

(27) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth & Co. (Publishers) Ltd., London, 1961.

most reactive molecules. These conclusions mean that relative reactivity measurements of $C_2O(X^3\Sigma)$ with the olefins should be the same regardless of the source of C_2O .

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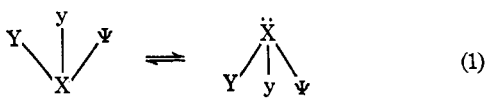
Inversion Barriers of Pyramidal (XY_3) and Related Planar ($=XY$) Species¹

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Abstract: Barriers to inversion, V_i , of 46 pyramidal (XY_3) ions and molecules have been evaluated by the method of Costain and Sutherland, and Weston. A valence force field is used, and the potential function has the form $V = 1.5k_1(\Delta l)^2 + 1.5k_2(\Delta\alpha)^2$. The input data for this model are the vibration frequencies (ν_1, ν_2) and bond parameters (l_{XY}, α). Some of the values of V_i in kcal/mole are: $(CH_3)_3N$, 7.5; H_3O^+ , 1-2; $(CH_3)_3O^+$, 11-26; CH_3^- , 6-12; $(CH_3)_3C^-$, 8-14; ClO_3^- , 49; SO_3^{2-} , 62. These barriers turn out to be most sensitive to changes in ν_2 and the YXY angle (α). Our results indicate why it has not been possible to prepare optically active carbanions and provide a rationale for the existence of configurationally stable phosphines, arsines, etc. The model has tentatively been extended to nonplanar cyclic species, and planar species which can undergo in-plane inversion (wagging). Thus, ethylenic, cyclopropyl, and cyclobutyl anions, as well as their isoelectronic nitrogen analogs, have been examined. Applications to mechanistic problems are discussed.

Barriers to intramolecular motions which lead to inversion are intimately related to the configurational identity of a molecule. The inversion barrier between two potential energy minima with the concomitant energy splitting, ΔE_n , of the vibrational energy levels in ammonia is a familiar example.^{2,3} Of course, when different groups are attached to an atom X in a pyramidal-like molecule XY_3 , we can write D and L forms⁴



Besides the ammonia analogs, e.g., PF_3 , $SbBr_3$, there are anions, e.g., CH_3^- , $(CH_3)_3Si^-$, ClO_3^- , TeO_3^{2-} , and cations, e.g., $(CH_3)_3S^+$, H_3O^+ , in which three groups and one electron pair are attached to one atom. We presume that all of these species are pyramidal and possess barriers to inversion. In respect to the configuration of the trivalent atom, some small ring species (1-4), e.g., cyclopropyl anions, aziridines, protonated ethylene oxides, or sulfides, etc., are obviously close kin

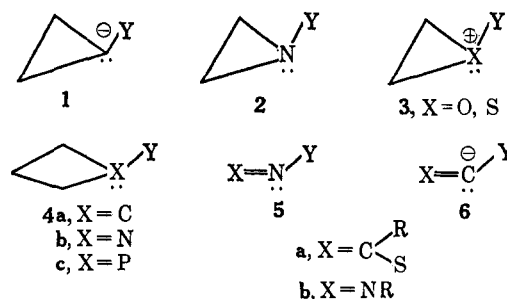
(1) Supported in part by the Petroleum Research Fund of the American Chemical Society; inquiries should be addressed to S. I. M.

(2) C. H. Townes and A. L. Schalow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chapter 12.

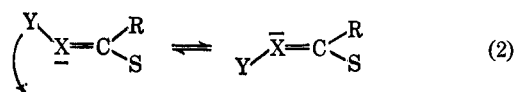
(3) G. Herzberg, "Molecular Spectra and Molecular Structure II," D. Van Nostrand, Inc., New York, N. Y., 1945: (a) pp 221-227; (b) pp 154-157, 162-165, 175-177.

(4) (a) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 88; (b) R. L. Shriner, R. Adams, and C. S. Marvel in "Organic Chemistry," Vol. 1, 2nd ed, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp 410-412, and Chapter 4 in general.

to these pyramidal species. And it does no real violence to the notion of inversion to include types 5 and 6,



or alkenides, imines, oximes, imido ethers, azoxy and azo compounds, etc., provided that they isomerize by in-plane wagging,⁵ e.g.



The barrier restricting inversion, V_i , has been associated both with the tunneling of the apical electron pair and with the deformation required to make the pyramid coplanar.^{2,3,6-10} Both aspects of the process

(5) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(6) J. F. Kincaid and F. C. Henriques, Jr., *ibid.*, **62**, 1474 (1940).

(7) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

(8) (a) R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954); (b) private communication, June 1954.

(9) (a) T. P. Norris and J. Dowling, *Can. J. Phys.*, **39**, 1220 (1961); (b) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (c) K. Toyoda, *Bull.*

are clearly different from rotations around bonds or pseudo-rotations in cyclic hydrocarbons.¹¹ There are cases, however, in which both rotation and inversion are possible. Thus, *all* of the conformations of methanol, hydrazine, methylamine, hydrogen peroxide, and analogs, and *some* of the conformations of cyclic systems containing oxygen and sulfur, are accessible either by inversion or by rotation, or by both.¹¹ Indeed, a distinction in these cases may not be feasible or meaningful, though one, in fact, might be tempted to ascribe "inversion-like" or "rotation-like" motions to these degenerate systems. In this paper, our main concern is with species which can invert as in eq 1 and 2.

With regard to their configurational integrity, the species of interest form a mixed group: some are stable and isolable; some are detectable as transients; some are transients but undetectable. The height of the barrier is related to the stereochemical stability. This is a quantity which is often unavailable, but which is often critically necessary in designing a stereospecific synthesis or mechanism. A schematic potential energy diagram for process 1 or 2 is shown in Figure 1. In this paper, we shall provide estimates of V_i .

A Model for Inversion Barriers

Kincaid and Henriques were perhaps the first to consider V_i and configurational stability together for a model species XY_3 . Using the relations

$$V = kx^2/2 \quad (3)$$

$$k = 4\pi^2\nu^2\mu \quad \mu = 3M_XM_Y/(3M_Y + M_X) \quad (4)$$

where V is the potential energy, x is the height of the pyramid, M_X and M_Y are the masses of groups (atoms) X and Y, and ν is the frequency leading to inversion, they calculated V_i for several molecules.⁶ As indicated in Figure 1, their parabolic potential function tends to overestimate V_i . Some of their predicted values in kcal/mole were: ammonia, 11; trimethylamine, 15; N-methylaziridine, 38; phosphine, 47. These may be compared with the substantially lower V_i calculated by Weston⁸ or by us (Table I). Now, Kincaid and Henriques were aware of this deficiency, but they tended to minimize its importance. For example, they suggested that N-alkylaziridines should be resolvable into optical isomers. Subsequently, several research groups made a search for such isomers, an effort which was frustrating, though perhaps instructive.¹²

In 1952, Costain and Sutherland (C.S.) showed that a valency force field adequately described the inver-

Chem. Soc. Japan, Pure Chem. Sect., **79**, 1198 (1958); (d) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962); (e) N. I. Bagdanskis and M. O. Bulanin, *Opt. Spectry.* (USSR), **19**, 128 (1966).

(10) Quantum mechanical calculations and estimates of inversion barriers have been reported: (a) for NH_3 , B. D. Joshi, *J. Chem. Phys.*, **43**, S40 (1965), and references cited; (b) for H_3O^+ , D. M. Bishop, *ibid.*, **43**, 4453 (1965); (c) for $NH=NH$, G. W. Wheland and P. S. K. Chen, *ibid.*, **24**, 67 (1956); J. Alster and L. A. Burnelle, *J. Am. Chem. Soc.*, **89**, 1261 (1967).

(11) (a) S. I. Miller, *J. Chem. Educ.*, **41**, 421 (1964); (b) T. Kasuya and T. Kojima, *J. Phys. Soc. Japan*, **18**, 364 (1963); (c) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960); M. T. Rodgers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (d) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 153 (1966).

(12) (a) P. E. Fanta in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, p 528; (b) H. M. Kissman and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 4317 (1952); (c) O. Paris and P. E. Fanta, unpublished results.

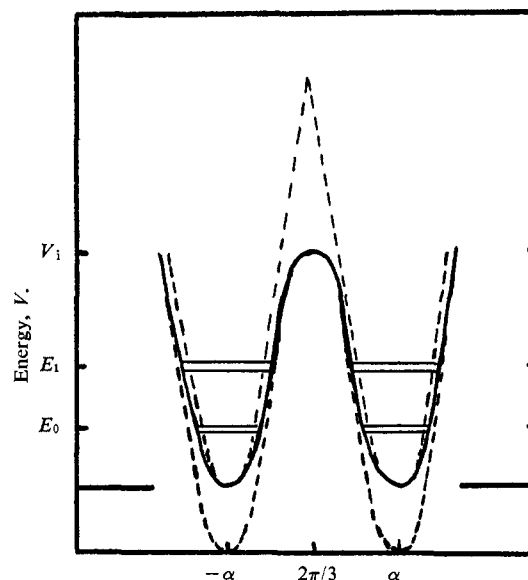


Figure 1. Potential energy for the inversion of pyramidal XY_3 (solid line). V_i is the barrier to inversion, α is the YXY equilibrium angle. The energy splittings (E_0 , E_1 , etc.) are exaggerated. The potential energy of an harmonic oscillator is given by the upper broken line. The lower broken line indicates the condition of strong solvation of the ground-state (polar) species, e.g., in the liquid (ref 9e).

sion process in ammonia.⁷ Here

$$V = \frac{1}{2}[k_1(\Delta l)^2 + k_\delta(\Delta\alpha)^2] \quad (5)$$

where Δl is the change in the bond length of XY , and $\Delta\alpha$ is the change in the bond angle YXY for pyramidal XY_3 . The force constants, k_1 and k_δ , are obtained from expressions involving ν_1 and ν_2 , the symmetric stretching and bending frequencies, respectively. From the symmetry coordinates involving ν_1 and ν_2 , one can relate Δl to $\Delta\alpha$ and thus obtain (see Appendix)

$$V = K(\Delta\alpha)^2 \quad (6)$$

and

$$V_i = K[(2\pi/3) - \alpha]^2 \quad (7)$$

where α is the equilibrium YXY bond angle.

Later, Weston used the C.S. approach and estimated V_i for 13 pyramidal molecules.⁸ In both papers,^{7,8} the calculations for ammonia generated $V_i = 5.9$ kcal/mole and vibrational energy splittings, ΔE_n (Figure 1), which agreed with the experimental values.

The matter of configuration was treated in two ways by Weston. Electron-pair tunneling from a given level could take place in a time τ_n given by

$$1/\tau_n = 2\Delta E_n c \quad (8)$$

where ΔE_n is the splitting in cm^{-1} , and c is the velocity of light. Thus, the observed values $\Delta E_0 = 0.79$ and $\Delta E_1 = 3.9$ cm^{-1} give $\tau = 2.5 \times 10^{-11}$ and 4.3×10^{-12} sec, respectively for ammonia. The rate constant for tunneling is

$$k_t = \frac{c \sum_n \Delta E_n \exp[-h\nu_2(n + 1/2)/kT]}{\sum_n \exp[-h\nu_2(n + 1/2)/kT]} \quad (9)$$

in which ΔE_n is related in a more or less complex fashion to V .^{8,9} Alternatively and more usually, the frequency of crossing over the barrier is assumed to take the form

$$1/\tau = k = Ae^{-V_i/RT} \quad (10)$$

Table I. Inversion Barriers, V_i , of Pyramidal Species^a

XY ₃	<i>l</i> , Å	α , deg	ν_1 , cm ⁻¹	ν_2 , cm ⁻¹	$k_1 \times 10^8$, dynes/cm	$k_2/l^2 \times 10^4$, dynes/cm	<i>K</i> , kcal/mole radian ²	V_i , kcal/mole	Ref
CH ₃ ⁻	1.09	105	2800	1250	4.4669	5.9366	152.6	10.5	<i>b</i>
CH ₃ ⁻	1.09	105	2800	1300	4.4661	6.4221	165	11.3	<i>b</i>
CD ₃ ⁻	1.09	109.5	2258	720	5.70336	4.3297	111	3.7	
CD ₃ ⁻	1.09	105	2258	720	5.5850	3.4089	87.7	6.0	
(CH ₃) ₃ C ⁻	1.54	105	720	320	2.5342	2.6556	159	10.9	<i>b</i>
SiH ₃ ⁻	1.48	109.5	2180	970	2.7882	5.1183	242	8.1	<i>c</i>
(CH ₃) ₃ Si ⁻	1.87	109.5	625	223	2.8951	2.0251	155	5.2	<i>c</i>
GeH ₃ ⁻	1.59	109.5	2106	931	2.6216	4.9765	272	9.1	<i>d</i>
(CH ₃) ₃ Ge ⁻	1.945	109.5	592	188	2.8967	2.0743	170	5.7	<i>d</i>
GeCl ₃ ⁻	2.2	108	320	162	1.739	0.2473	271	12	<i>d</i>
SnCl ₃ ⁻	2.32	108	247	128	1.6359	1.8392	217	9.5	N
SnBr ₃ ⁻	2.45	109.5	211	83	1.6699	1.3514	180.5	6.06	N
NH ₃	1.014	106.77	3539 ^e	1055 ^e	7.2146	4.7146	104.7	5.58	W
NH ₃ (s)	1.012	106.67	3223	1060	5.9817	4.7348	104.8	5.67	N
ND ₃	1.014	106.77	2524 ^e	803 ^e	7.1162	4.7805	106.3	5.67	W
ND ₃	1.011	106.7	2420	747.5	6.5404	4.1273	91.3	4.91	N
ND ₃ (s)	1.011	106.7	2318	815	5.9973	4.9092	108.6	5.85	N
NT ₃	1.011	106.7	2016	647	6.5942	4.1494	91.9	4.95	N
¹⁵ NH ₃	1.011	106.7	3355	943.5	6.4191	3.7937	83.8	4.51	N
(CH ₃) ₃ N	1.470	109.0	827	365	4.1146	3.9807	202	7.46	W
NF ₃	1.40	105	1032	642	6.993	1.192	609	42	N
NF ₃	1.40	110	1032	642	7.110	1.589	915	29	N
NCl ₃ ⁻	1.76	106	652	390	4.6928	5.6476	443	26	<i>f</i>
PH ₃	1.415	93.3	2323	991	3.11362	2.91229	126	27	W
PH ₃	1.415	93.3	2460 ^e	1070 ^e	3.49164	3.39519	147	32	W
PH ₃	1.420	93.5	2327	991	3.1250	2.9239	127	27	N
PD ₃	1.416	93.1	1694	730	3.2148	2.9745	129	28	N
PT ₃	1.41	93	1398	623	3.1841	2.0825	133	30	N
(CH ₃) ₃ P	1.87	100	653	263	2.7837	2.1425	168	20	W
PF ₃	1.55	104	892	487	6.2129	9.8411	578	45	W
PCl ₃	2.040	100.0	507	260	2.3492	4.6227	613	74	N
PCl ₃	2.040	100.0	510	257	2.4336	4.3978	558	68	W
PBr ₃	2.180	100.08	400	116	2.4669	1.4048	167	20	W
PI ₃	2.46	100.0	300	111	1.5548	1.8989	354	43	N
AsH ₃	1.523	91.5	2209	974	2.8610	2.8181	141	34	W
AsH ₃	1.519	91.83	2122	906	2.6405	2.4534	122	30	N
AsD ₃	1.514	91.52	1534	660	2.7232	2.5229	125	31	N
AsT ₃	1.510	91.6	1256	553	2.6443	2.5932	128	31	N
(CH ₃) ₃ As	2.05	96.0	568	223	2.4462	1.8182	167	29	W
AsF ₃	1.712	101.0	707	341	4.7559	5.6900	368	41	N
AsCl ₃	2.161	98.40	412	194	2.5353	2.7407	294	42	N
AsBr ₃	2.330	100.5	284	128	1.9856	2.2597	313	36	N
AsI ₃	2.550	101.0	216	94	1.3211	1.8764	364	40	N
SbH ₃	1.707	91.30	1891	782	2.1067	1.8283	115	29	N
SbD ₃	1.702	90.93	1359	561	2.1576	1.8387	115	30	N
SbT ₃	1.70	90.9	1118	466	2.1725	1.8728	117	30	<i>g</i>
(CH ₃) ₃ Sb	2.150	96.00	513	188	2.1172	1.4238	143	25	N
SbCl ₃	2.360	95.20	377	164	2.3510	2.1030	259	49	N
SbBr ₃	2.510	97.00	254	101	1.9303	1.4779	214	34	N
H ₃ O ⁺	1.020	116.0	2800	1150	4.6187	1.5185	341	1.7	<i>i</i>
H ₃ O ⁺	0.960	117.0	3285	1175	6.3705	2.0610	410	1.1	<i>h</i>
D ₃ O ⁺	0.960	117.0	2455	785	7.0703	1.5964	318	0.87	<i>h</i>
H ₃ O ⁺	1.00	115	2600.7	1229.2	3.976	0.1423	307.5	2.34	<i>j</i>
D ₃ O ⁺	1.00	115	1849.9	931.0	3.976	0.1423	308.0	2.34	<i>j</i>
(CH ₃) ₃ O ⁺	1.49	105	1200	450	8.3499	5.5128	280	19	<i>b</i>
(CH ₃) ₃ S ⁺	1.820	109.08	654	285	3.1938	3.4481	253	9.2	W
(CH ₃) ₃ S ⁺	1.830	103.0	654	285	2.9216	2.7312	205	18	W
(CH ₃) ₃ S ⁺	1.820	100.0	654	285	2.8015	2.5593	191	23	W
(CH ₃) ₃ S ⁺	1.830	100.08	654	285	2.80462	2.56311	191	23	W
SO ₃ ²⁻	1.500	105.0	967	620	6.3780	1.5409	906	62	N
SeO ₃ ²⁻	1.760	99.3	807	432	5.3093	7.8357	537	70	N
TeO ₃ ²⁻	1.800	99.0	758	364	4.9590	6.0846	429	58	N
ClO ₃ ⁻	1.490	106.7	930	610	6.2667	1.6245	913	49	N
BrO ₃ ⁻	1.780	111.8	806	421	5.7847	1.3505	932	19	N
IO ₃ ⁻	1.820	99.0	779	340	5.2316	6.9823	504	68	N

^a Bond parameters and vibrational frequencies taken from Weston⁸ are labeled W. In a few cases, his V_i values had to be changed. Normally, bond parameters were taken from ref 15, and vibration frequencies were taken from ref 16; these were labeled N. In the remaining cases, frequencies and bond dimensions were taken from other sources or were estimated from closely related species. ^b The input data were varied. See Table II and the relevant figure (2-5). ^c Data on the silanes are in ref 15 and in D. F. Ball, P. L. Goggin, D. C. McKean, and L. A. Woodward, *Spectrochim. Acta*, **16**, 1358 (1960). ^d Data on the germanes: ref 15; F. Glockling, *Quart. Rev.* (London), **20**, 45 (1966); M. Delwaille and F. Francois, *Compt. Rend.*, **228**, 1585 (1949). ^e Anharmonic frequencies. ^f G. E. Moore and R. M. Badger, *J. Am. Chem. Soc.*, **74**, 6076 (1952). ^g G. DeAlti, G. Costa, and Y. Galasso, *Spectrochim. Acta*, **20**, 965 (1964). ^h K. Heinzinger and R. E. Weston, Jr., *J. Phys. Chem.*, **68**, 744 (1964). ⁱ Reference 10b. ^j See Appendix.

Two serious problems may arise here. For barriers lower than, or about equal to, that of ammonia, quantum-mechanical tunneling must be taken into account, as in eq 9. Secondly, it should be noted that although eq 10 is formally suitable, the standard assumption that $A \simeq 10^{12}$ – 10^{13} sec $^{-1}$ is uncertain and could be misleading. If the ammonia values of τ and $V_i = 5.9$ kcal/mole are used in eq 10, the calculated $A = 1.5 \times 10^{14}$ sec $^{-1}$ is somewhat high. In fact, a range of A factors, 10^5 to 10^{13} , has been reported for compounds which invert at a nitrogen center.^{13,14} As a criterion of "resolvability," Weston assumed that an optical isomer should have a half-life of 1–2 hr at 27°; with $A \simeq 10^{13}$ sec $^{-1}$ in eq 10, this leads to $V_i > 22$ kcal/mole. It is convenient to use this "energy criterion," and we shall use it frequently. Here, one should not lose sight of the possibility of tunneling and the uncertainty in the preexponential or entropy term of eq 10, difficulties which are not dealt with in the C.S. model. However, when a real, as opposed to a calculated, stability of a molecule is involved, it is more desirable to use a "rate criterion," $k = 10^{-4}$ sec $^{-1}$, whenever possible, and by-pass the problem in assigning A .

Barriers for isolated species are obtained by the C.S. method, but many species of interest are, of course, present in a condensed phase. Bagdanskis and Bulanin have shown analytically how V_i might be altered (see Figure 1) if a pyramidal species is treated as a polarizable dipole in a continuous dielectric (Onsager field). Both the calculations and the observations indicate that ammonia inversion is inhibited in a polar medium, a matrix, or in a nonpolar solvent.^{9e} Analogous solvent effects on other inversion rates at a nitrogen center have been noted: for a 2,3-diazabicyclo-[2.2.1]heptane, the change in medium from pentane to water increases the barrier free energy by 2.5 kcal/mole;^{13f} for 1,2,2-trimethylaziridine in three mediums, the inversion rates were lower in the more polar solvents, although compensating effects in V_i and A were observed.^{13b} N-Benzyl-O,N-dimethylhydroxylamine is exceptional, for the change from *n*-hexane ($\epsilon = 2$) to methylene chloride ($\epsilon = 9$) causes a decrease in V_i of 3.5 kcal/mole and an almost compensating decrease in A of $10^{2.8}$; this was explained on the basis that the pyramidal form was *less* polar.^{13a} Clearly, solvent effects on V_i and A , which can be large, demand a fairly detailed theory for their explanation; obviously, such a theory goes beyond the C.S. model and probably will have to improve on the dipole model.^{9e}

Fairly elaborate potential functions have been used to describe the motions of ammonia.^{9d} One might wonder then whether the relatively simple C.S. model could be at all useful. Its basis is a quadratic potential function. Yet it applies to ammonia in which deformations of *ca.* 13° are required and has also been applied

(13) (a) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); (b) A. Lowenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960); (c) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958); (d) I. J. Bardos, C. Szantay, and C. K. Navada, *ibid.*, **87**, 5796 (1965); (e) A. L. Logethetis, *J. Org. Chem.*, **29**, 3049 (1964); (f) J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).

(14) (a) In nmr studies, the preexponential factor A may be taken as 6.25×10^{12} sec $^{-1}$ at 25°, but unless A can be measured directly, it would seem prudent to use only the experimentally observed quantities, k , or line coalescence temperatures rather than eq 10;^{13e} (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, Chapter 9; (c) E. F. Caldin, "Fast Reactions in Solution," Blackwell Scientific Publications, Oxford, 1964, Chapters 1, 11.

to the problem of configurational stability of pyramidal molecules in which $\Delta\alpha \simeq 29^\circ$, with apparent success.^{7,8} On this basis, Weston, concluded that the isolation of optical isomers of trivalent nitrogen compounds was not feasible, but that the isolation of similar compounds of other group V elements should be possible. These conclusions turned out to be correct.⁸

Having described the major problems in the C.S. model, we now wish to apply it in depth. At this point, we shall be satisfied if it generates reasonable trends in V_i . Accurate predictions will presumably come later with more sophisticated models.

Inversion Barriers

Our own interest in inversion barriers began with the question of the steric stability of carbanions.⁵ It was natural to expand the work to include pyramidal species for which bond geometry and vibration frequencies were available or could reasonably be estimated. Since a computer was available, it was a simple matter to vary the parameters so that limiting conditions for the C.S. model could be defined and the critical factors governing V_i discerned.

The input data and the calculated results for molecules and ions are given in Table I. As a check on our computer program, we repeated Weston's calculations⁸ and usually obtained reasonable agreement. In some cases, more recent values of bond parameters or vibration frequencies have become available so that these were also used.^{15,16} Occasionally, ν_1 , ν_2 , and α had to be estimated by analogy with related molecules.

Before coming to the results, let us consider the factors that influence the magnitude of V_i . These are separated in Figures 2–5, where one set of parameters is taken as "standard." Then, the separate dependence of V_i on each factor, ν_1 , ν_2 , α , and sometimes on l , M_X , and M_Y , is indicated, as each is varied from the standard.

The XY bond length (l) and stretching frequency (ν_1) exert little or no influence on V_i (Figures 2 and 4). Therefore, the uncertainties in these quantities, whether measured or estimated, pose few problems with regard to the evaluation of V_i .

That M_X and M_Y could be useful independent variables struck us as unrealistic, at first. After all, the masses of the groups are fixed as soon as the species is identified. However, the calculations with variable M_X and M_Y gave us increased understanding of certain trends in V_i . Figure 2 showed that V_i is moderately sensitive to M_X for low M_X but highly sensitive to M_Y throughout the range of M_Y . The latter point is well illustrated by trimethylphosphine and trichlorophosphine, which differ chiefly in their M_Y property and therefore in V_i . An estimate of V_i for other phosphines, triethyl- or methylethylpropyl-, say, would be another application of M_Y used as a variable. One cautionary note: as M_Y increases in a real series, α also increases; that is, the mass effect may be counteracted by a steric factor, e.g., NH₃ (106.6°), (CH₃)₃N (108°), (C₂H₅)₃N (113°).¹⁵

Together, ν_2 and α constitute the prime influences on V_i (Figures 2–5). It is natural that V_i should increase

(15) L. E. Sutton, Ed., "Tables of Interatomic Distances," The Chemical Society, London, 1958, 1965.

(16) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

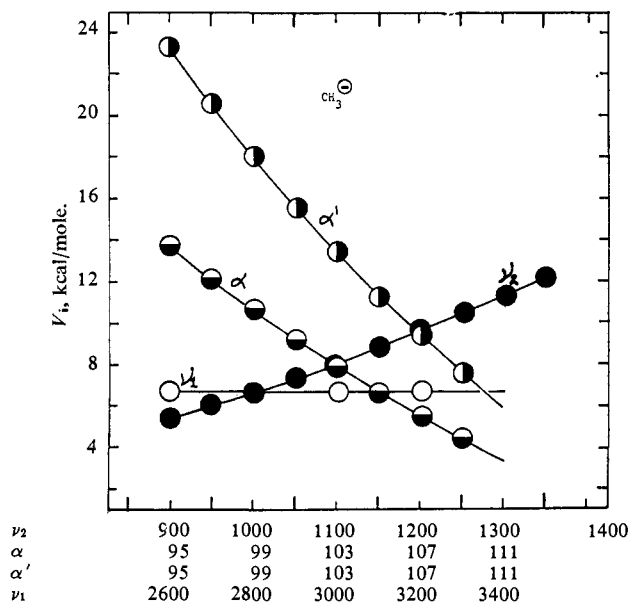
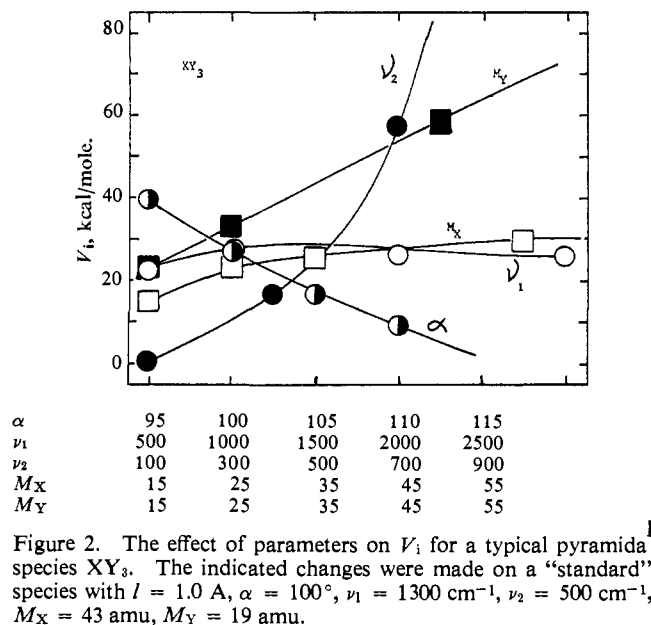


Figure 3. The effect of parameters on V_i for CH_3^- . The indicated changes were made on a standard CH_3^- with $l = 1.09$ A, $\alpha = 105^\circ$, $\nu_1 = 2800$ cm^{-1} , $\nu_2 = 1000$ cm^{-1} . In addition, ν_2 was set at 1300 cm^{-1} , and variations in α were examined; this set of α 's is primed

as it becomes more difficult to make XY_3 coplanar; what we stress here is the sensitivity of V_i to these quantities in the C.S. model. Indeed, when α or ν_2 are uncertain to begin with, one essentially chooses V_i with the assignment of α or ν_2 . The methide, trimethylcarbanion, and trimethyloxonium species were of particular interest to us. Because α , ν_1 , and ν_2 were unavailable, we tested a whole range of values, and it became clear that one must be able to limit α and ν_2 before the present model can be used to obtain useful estimates of inversion barriers (see Figures 3-5).

Having set out the practical problems associated with the C.S. evaluation of V_i , we turn to the calculations of Table I. For the great majority of the species examined, α and ν_2 are known so that the calculated V_i values are reliable. In a few cases, bond properties had to be estimated, but we believe the calculated V_i

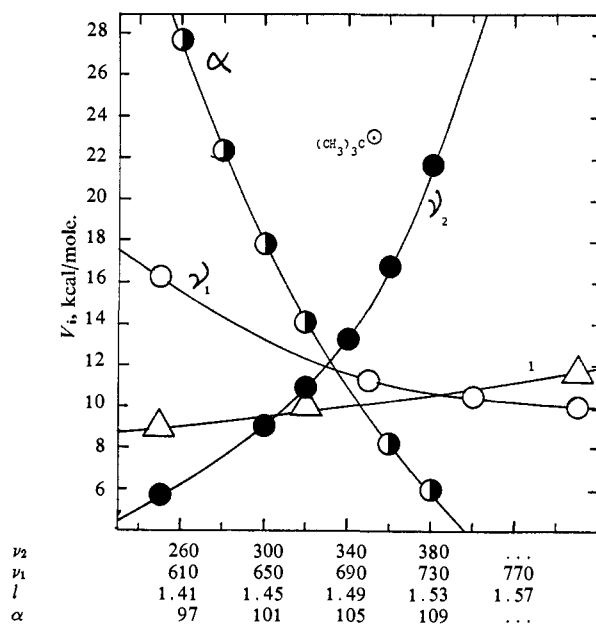


Figure 4. The effect of parameters on V_i for $(\text{CH}_3)_3\text{C}^-$. The indicated changes were made on a standard $(\text{CH}_3)_3\text{C}^-$ with $l = 1.54$ A, $\alpha = 105^\circ$, $\nu_1 = 720$ cm^{-1} , $\nu_2 = 320$ cm^{-1} .

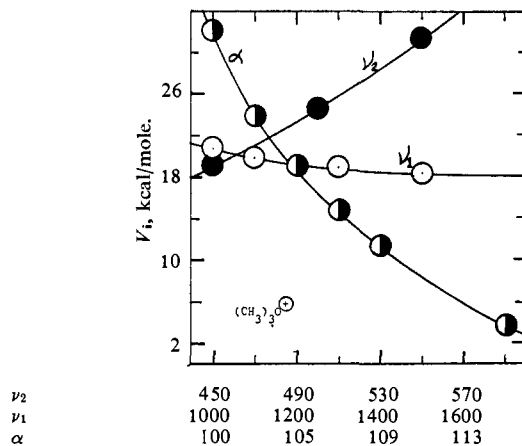


Figure 5. The effect of parameters on V_i for $(\text{CH}_3)_3\text{O}^+$. The indicated changes were made on a standard $(\text{CH}_3)_3\text{O}^+$ with $l = 1.49$ A, $\alpha = 105^\circ$, $\nu_1 = 1200$, $\nu_2 = 450$.

values cannot be grossly in error. We could not, however, be so confident about CH_3^- , H_3O^+ , $\text{C}(\text{CH}_3)_3^-$, $(\text{CH}_3)_3\text{O}^+$, and a range in V_i was established for some of them (Table II). Nevertheless, the broad conclusion that emerges is that pyramidal species involving the second period elements carbon, nitrogen, oxygen should not have resolvable optical isomers, or $V_i < 22$ kcal/mole. On the other hand, many pyramidal species of elements beyond the second period should not invert readily, or $V_i > 22$ kcal/mole. Failure to find optically active amines or carbanions and successful isolation of active phosphines, phosphites, arsines, sulfoxides, and sulfonium salts are consistent with this conclusion.⁴

It should not be supposed, however, that all pyramidal species of elements beyond the second period will be resolvable into optical antipodes and those in it will not. V_i for silyl, germyl, or tribromotin(II) anions are ≤ 9 kcal/mole. In these cases, our assigned α values were relatively high ($\Delta\alpha$ is small), and ν_1 and ν_2 were

Table II. Barriers, V_i in kcal/mole, of Pyramidal Species, YX_3^a

CH_3^-	10.5 (6-12)	NH_3	5.58	AsH_3	34	H_3O^+	2.34 (1.1-4.8)	ClO_3^-	49
$C(CH_3)_3^-$	10.9 (8-14)	NF_3	42 (18-42)	$As(CH_3)_3$	29	$(CH_3)_3O^+$	19.2 (11-26)	BrO_3^-	41 (19-87) ^b
SiH_3^-	8.1	$N(CH_3)_3$	7.46	AsF_3	40	$S(CH_3)_3^+$	23 (9-23)	IO_3^-	68
$Si(CH_3)_3^-$	5.2	NCl_3	26	$AsCl_3$	42	SO_3^{2-}	62		
GeH_3^-	9.1	PH_3	27 (21-31)	$AsBr_3$	36	SeO_3^{2-}	70		
$Ge(CH_3)_3^-$	5.7	$P(CH_3)_3$	20.4	AsI_3	40	TeO_3^{2-}	60		
$GeCl_3^-$	11.9	PF_3	45	SbH_3	29				
$SnCl_3^-$	9.5	PCl_3	74	$Sb(CH_3)_3$	25				
$SnBr_3^-$	6.1	PBr_3	20	$SbCl_3$	49				
		PI_3	43	$SbBr_3$	34				

^a Typical data for the evaluation of V_i are given in Table I. Arbitrary variations of these data, as in Figures 2-5, led to the indicated range in V_i .¹⁶ ^b The reported value of α for BrO_3^- is implausibly low. Our estimate of $V_i \approx 41$ is based on $\alpha \approx 105^\circ$.

low, so that V_i had to be low. This may be typical of other "heavy" species. Indeed, V_i for $(ClHg)_3O^+$ is likely to be close to zero, since the reported α is close to 120° .¹⁵ On the other hand, V_i for two nitrogen trihalides seems to be >20 kcal/mole, so that a resolvable pyramidal nitrogen species is conceivable.

There are a fair number of species whose resolvability may be borderline. In these cases, the racemization process coincides, fortunately, with the nmr time scale, where free-energy barriers (G_i) of ca. 10-20 kcal/mole can be measured.¹⁴ Incidentally, one need not isolate a compound to have evidence of its existence. The inversion doubling of ammonia is observed in the microwave region; the inversion of aziridines can be followed by nuclear magnetic resonance (nmr) spectroscopy. Therefore, one can say that an isomer is "detectable" and discuss its lifetime in relation to the time scale of the operating technique. In this regard, free uncomplexed carbanions, oxonium ions, or trisubstituted tin(II) anions, to cite several, are interesting possibilities for nmr studies.

Experimental Tests of the C.S. Model

Apart from V_i for ammonia, there are few facts to go on, where nitrogen is the apex atom. Relatively low inversion barriers (kcal/mole) have been reported for hydrazine (2.8),^{11b} formamide (1.1),^{11c} cyanamide (2),^{11d} nitramide (2.7),^{11d} and aniline (0.3).^{11d} Saunders and Yamada give $k_i = 2 \times 10^5 \text{ sec}^{-1}$ for methyl-dibenzylamine at 25° ;¹⁷ by eq 10 ($A \approx 10^{13}$) we estimate $V_i \sim 11$ kcal/mole. On the nmr time scale, the inversions of molecules such as $C_6H_5CH_2(CH_3)NZ$ ($Z = OH, Cl, N(CH_3)_2, N(CH_3)_3^+$) are all too fast to measure, but when $Z = OCH_3$ $\log A = 10-12.8$ and $V_i = 9.4-12.8$ kcal/mole, depending on the solvent.^{13a} Supporting evidence for this last observation comes from a report on the detection of inversion in O_3N_2N -triheptafluoro-*n*-propylhydroxylamine, $(n-C_3F_7)_2NOC_3F_7-n$.¹⁸ By comparison with the amine data, $V_i \approx 7$ kcal/mole for trimethylamine might seem low. It is plausible, however, that more complex amines would have higher barriers, for, besides inversion, there may be rotational barriers to overcome. There is in fact the case of *N*-tosylbenzoquinolone and similar compounds, for which the nmr technique indicates an unusually high order of stability.^{13a,19}

(17) M. Saunders and F. Yamada, *J. Am. Chem. Soc.*, **85**, 1882 (1963).

(18) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965).

(19) W. N. Speckamp, U. K. Pandit, and H. O. Huisman, *Tetrahedron Letters*, 3279 (1964); W. N. Speckamp, U. K. Pandit, P. K. Korver, P. J. Van Der Haak, and H. O. Huisman, *Tetrahedron*, **22**, 2413 (1966).

For the phosphines, our lowest calculated $V_i \approx 20$ kcal/mole for trimethylphosphine. This appears to be a lower limit, since the available data are all consistent with higher barriers. Qualitative data on di-*n*-perfluoropropylidodiphosphine,^{20a} octafluoro-1,4-diiodo-1,4-diphosphane,^{20b} 1-methylphospholenes,^{20c} 1-methylphosphorinans,^{20d} and 9-phenyl-9-phosphabicyclo-[6.1.0]nonatriene^{20e} and phosphites^{20f} indicate stability toward inversion. More directly, kinetic measurements on the racemization of optically active methyl-*n*-propylphenylphosphine yield an activation energy ≈ 29 kcal/mole ($t_{1/2} = 5.5$ hr in *n*-decane at 130°),^{21a} and nmr measurements ($125-200^\circ$) on 1,2-dimethyl-1,2-diphenyldiphosphine yield an activation energy of 26 kcal/mole.^{21b}

It appears that trisubstituted arsines, e.g., methyl-*n*-propylphenylarsine, are even more stable to inversion than the corresponding phosphines. The barriers are so high that photosensitization, e.g., with acetophenone, was used to impart sufficient energy (>60 kcal/mole) for the racemization.^{21c}

Evidence for barriers in acyclic carbanions may derive from organometallic compounds; indeed, the configurational stability of organometallic compounds has often been examined.^{22,23} Information may also come from other reactions, e.g., proton abstraction, decarboxylation, carbon-carbon bond fission, nucleophilic additions to alkenes, etc., in which such anions may be produced.²²⁻²⁵ But in these cases, as in any others in which carbanions are sought, the relation between the stability of some parent species and V_i may be far from simple: either the inversion process does not occur, or it is strongly influenced by the particular reaction conditions. Thus, there has been a

(20) (a) J. F. Dixon, *J. Chem. Soc.*, 777 (1965); (b) C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.*, **27**, 3584 (1962); (c) L. D. Quinn, J. P. Gratz, and R. E. Montgomery, *Tetrahedron Letters*, 2187 (1966); (d) L. D. Quinn and H. E. Shook, Jr., *ibid.*, 2193 (1966); (e) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966); (f) B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966).

(21) (a) L. Horner and H. Winkler, *Tetrahedron Letters*, 461 (1964); (b) J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, **88**, 3669 (1966); (c) L. Horner and W. Hofer, *Tetrahedron Letters*, 3323 (1966).

(22) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 3, 4.

(23) (a) M. Witanowski and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 737 (1966); (b) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *ibid.*, **87**, 2844 (1965); (c) G. Fraenkel and D. T. Dix, *ibid.*, **88**, 979 (1966).

(24) (a) H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966); (b) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 2176 (1966).

(25) S. Patai and Z. Rappoport, "The Chemistry of Alkenes," S. Patai, ed., Interscience Publishers, New York, N. Y., 1964, pp 525-546; D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960); P. K. Yonan and S. I. Miller, *J. Am. Chem. Soc.*, **79**, 5931 (1957); G. Modena, P. E. Todesco, and S. Tonti, *Gazz. Chim. Ital.*, **89**, 878 (1959).

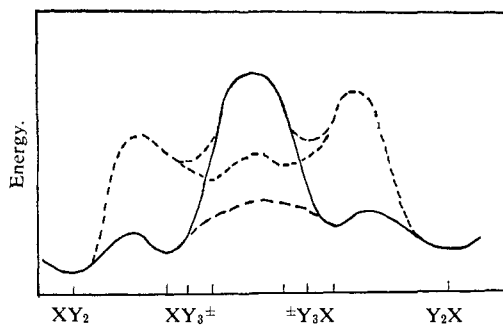
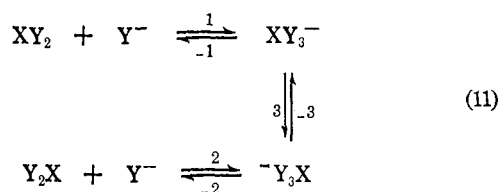


Figure 6. Schematic energy profile for inversion of an ion XY_3^- formed from neutral species XY_2 , as in eq 11. The ion may be D, *trans*, *syn*, etc.

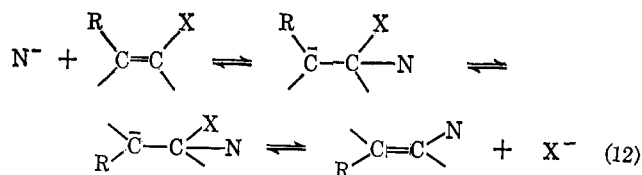
suggestion that some organometallic, *e.g.*, Grignard, reagents may be inverted by electrophilic attack, $RMg^+ + (RMgX)_2$.²³ In solvents of low polarity, ion aggregates will alter the stability of the carbanion and may provide alternate paths for isomerization. In short, if one is concerned with inversion of the free anion, one must make certain that the observations are relevant to it.

A minimum scheme which covers many possibilities for generating carbanions follows.



XY_2 and Y_2X are the isomeric forms (D and L, *cis* and *trans*, *syn* and *anti*, etc.) and Y^- stands for the charged species that must be added (or removed) to give a charged anion. Now, certain experimental results do allow of unambiguous interpretations of any system following eq 11; if racemization is rapid, then the upper limit $V_i \leq 22$ kcal/mole at 25°; if inversion is detectable by nmr, the limit might be $V_i \leq 18$ kcal/mole at 25°; if no racemization is observed, then V_i is undetermined. Isotopic or other labeling of steps 1 and 2 in eq 11 provides for further refinement: if the ratio of exchange to racemization is given by k_{-1}/k_{rac} , then $E_a(rac) > V_i > RT \ln k_{-1}/k_{rac}$. An energy profile for scheme 11 is given in Figure 6. This should be particularly useful in displaying the possibilities inherent in scheme 11 and in setting limits on V_i .

Consider the data bearing specifically on carbanion stability. The racemization of certain Grignard reagents, *e.g.*, 3,3-dimethylbutyl- and 2-methylbutylmagnesium halides, has been followed by nmr, and E_a falls in the range 11–20 kcal/mole.²³ If scheme 11 were involved, then $V_i \leq 11$ –20 kcal/mole. Cram, *et al.*, have reported extensively on the generation of carbanions from optically active precursors.²² The published rate studies often indicate $k(\text{retention})/k(\text{racemization}) = 0$; this only means that we have the lower limit $V_i > 0$ kcal/mole. On the other hand, $k(\text{retention})/k(\text{racemization})$ often approaches 100. Taking this factor at 227°, which lies in the range of some of the work, we obtain another (not *the* other) limit $V_i \geq 5$ kcal/mole. Likewise, nucleophilic displacement of haloalkenes



proceeds chiefly with retention; isomerization appears to be a slower process.²⁵ Again, such data set only a low, lower limit on V_i . All of these data, $5 < V_i < 20$ kcal/mole, are consistent with the notion that free pyramidal carbanions are *not* resolvable.²² Our calculations for methide and trimethylcarbanion suggest that the barriers are indeed too low to admit of resolution (Tables I and II, Figures 3 and 4).

It does not seem necessary to comment on all of the entries in Tables I and II. In any case, the barriers of some of these species cannot be measured directly, and suitable analogs would have to be prepared. It is worth pointing out, however, that the oxonium ions (H_3O^+ , $(CH_3)_3O^+$) have the lowest calculated inversion barriers; this prediction should be tested.

Isotope Effects

To conclude our survey of pyramidal species we note that isotope effects on the calculated barriers turn out to be small (Table I). The minor differences in the values of V_i that turn up for isotopically substituted molecules are artifacts. That is, each molecule was treated independently and the available ν_1 , ν_2 , l , and α , whether observed or estimated, could then generate different force constants for isotopically substituted species. An alternate procedure would be to transfer force constants derived in one molecule containing protium to the others containing deuterium or tritium. In the C.S. model it turns out that Δl and $\Delta \alpha$ of eq 5 are almost mass independent so that there are no significant isotope effects on V_i . (Zero-point energy differences also do not figure here, since they remain constant in the C.S. model during inversion.) Hydronium and deuterium ions were interesting and critical examples: after adjusting ν_1 and ν_2 (see Appendix) to obtain similar force constants k_1 and k_2 , we could not detect a significant difference in their V_i (2.34 kcal/mole). Indeed, Norris and Dowling found it natural to assign a common V_i for all of the isotopically substituted ammonia species, before they calculated ν_2 and the inversion energy levels.^{9a} Moreover, the barriers to N-methyl and N-methyl- d_3 inversion in a bicyclic system were reported to be identical.^{13f}

There may be cases in which racemization by tunneling becomes the predominant mechanism for inversion. Here, striking effects of deuterium or tritium substitution for protium may show up in the racemization rate,^{2,8,9} but we know of no reports bearing on this point.

In view of these results, we were interested by a report in which an isotope effect on V_i of 4 kcal/mole was reported for nitrogen inversion of 2,2,3,3-tetramethylaziridine- d_1 .^{13d} Obviously, this large effect should be checked, for it appears to be at odds with previous data.

Inversion in Cyclics and Unsaturation

Because of the general interest in interconversions involving certain cyclic and unsaturated nitrogen compounds (2, 4, 5) as well as in the isoelectronic carbanions

Table III. Inversion Barriers for Cyclic and Unsaturated Species

Species ^a	No.	K , kcal radians ⁻² mole ⁻¹ ^b	$\Delta\alpha$, deg ^{b,c}	V_i (calcd), kcal/mole ^b	Species (obsd)	V_i (obsd), kcal/mole
CH ₃ ⁻		153	1	0.0465		
<i>c</i> -C ₄ H ₇ ⁻	4	102	(25)	(19)		
<i>c</i> -C ₅ H ₅ ⁻	1	102	(25)	(19)		
=CH ⁻	6	102	(35)	(38)	XCH=CX ⁻	>30 ^d
CR ₃ ⁻		159	1	0.0484		
<i>c</i> -(1-RC ₄ H ₆) ⁻	4	106	(25)	(20)		
<i>c</i> -(1-RC ₃ H ₄) ⁻	1	106	(25)	(20)		
=CR ⁻	6	106	(35)	(40)	C ₆ H ₅ CH=CC ₆ H ₅ ⁻	10–20 ^e
NH ₃		104.7	1	0.0319		
<i>c</i> -C ₃ NH ₇	4	69.8	(25)	(13)	N-Trifluoromethyl- oxazetidines	~10 ^f
<i>c</i> -C ₂ NH ₅	2	69.8	40 (27)	34 (15)	2,2,3,3-Tetramethyl- aziridine	11–15 ^g
=NH	5	69.8	(40)	(34)		
NR ₃		202	1	0.0615		
<i>c</i> -1-RC ₃ NH ₅	4	134.6	(20)	(16)		
<i>c</i> -1-RC ₂ NH ₄	2	134.6	(20)	(16)	N-Methylaziridines	5–12 ^h
=NR	5	134.6	(25)	(41)	N-Alkylimine	25–27 ⁱ
NF ₃		609	1	0.185		
=NF	5	406	65	(522)	FN=NF	32 ^j

^a The prefix *c* indicates a cyclic compound. ^b K or $2K/3$ was used according to eq 13. The K values were taken from CH₃⁻, (CH₃)₃C⁻, NH₃, (CH₃)₃N, Table I. Values in parentheses are uncertain. ^c $\Delta\alpha$ was usually chosen to yield plausible values of V_i . Values of $\Delta\alpha$ listed for azo compounds show wide variations: azomethane, $70 \pm 10^\circ$; azotoluene, 46° .¹⁵ ^d Reference 5. ^e Reference 28. ^f Reference 33. ^g Reference 13d. ^h Reference 13. ⁱ Reference 34b. ^j Reference 34d.

(1, 3, 6), it would be desirable to have estimates of V_i .²² The process of "inverting" these species (eq 2) is assumed to be similar to that of the pyramidal species. In the unsaturates, *e.g.*, azo compound or ethenide, there is an alternative mode of isomerization, namely, breaking of the π bond followed by rotation. Since activation energies for this mechanism generally lie in the range 40–60 kcal/mole,²⁶ internal rotation should not be competitive with in-plane inversion (eq 2) in the range of greatest interest (<35 kcal/mole).

The model we test is naïve. It is assumed that group Y of species 1–6 moves in the same fashion that it does in the pyramidal species. But because one angle has become fixed, at *ca.* 60° in 1–3, 90° in 4, and 0° in 5 and 6, we rewrite eq 6 as

$$V = \frac{2}{3}K(\Delta\alpha)^2 \quad (13)$$

In this context, we can transfer the K values from the pyramidal species in Table I to the cyclics and unsaturates. In Table III, we list the energies required for inversions of several interesting species. Since few bond angles, α , are known, the calculations simply define V_i in terms of an arbitrarily chosen bond angle and an available potential function. It should be clear, however, that our listed α or $\Delta\alpha$ values are on the low side, thus introducing a compensating error in the overall estimate of V_i .

It is emphasized that these extrapolations from pyramidal species involve all of the deficiencies of the Kincaid–Henriques approach to barrier estimation.⁶ As with eq 3, calculations based on eq 13 are likely to overestimate V_i (see Figure 1). At this time, we have only this crude model and propose that the figures in Table III are to be regarded as gross, qualitative, unrealistic, etc. Nevertheless, since many workers are currently engaged in examining barriers or mechanisms involving these species, we believe that the calculated

barriers of Table III have some virtue and considerable interest.

Consider first the cyclic carbanions. Cram has recently reviewed information on cyclobutyl and cyclopropyl organometallic species.²² The fact that such compounds are *not* racemized on the nmr time scale or in certain chemical reactions, *e.g.*, hydrolysis, carbonation, etc.,²⁷ does not tell us much about V_i . Even when racemization of an optically active center does occur, the uncertainty in the mechanism again makes estimates of V_i uncertain. One does, however, get the impression that if carbanions are involved in the isomerization of these cyclic species, the inversion barriers would be somewhat higher than those found or estimated for acyclic analogs. Therefore, the results in Table III have been made consistent with this impression.

For ethenide ions, however, the experimental results seem more definite. Hunter and Cram found that the *t*-butoxide-catalyzed deuteration of *cis*-stilbene was 2500 times that of isomerization at 146°. ²⁸ Using Figure 6, we estimate that $V_i > 9$ kcal/mole. Several workers have found that arylvinyl lithium reagents showed partial stereochemical stability in benzene-ether (–40 to 25°), *i.e.*, $\tau \approx 30$ min.²⁹ Such observations suggest that $V_i \leq 20$ kcal/mole so that 10–20 kcal/mole might be taken as the range for the barrier of 1,2-diphenylethenide. Another kind of example is found in those ethenes, *e.g.*, 1,2-dihaloethanes⁵ or 1,1-diaryl-2-haloethenes,^{30–32} whose 2-protons exchange

(27) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 2283 (1964), and previous work.

(28) D. H. Hunter and D. J. Cram, *ibid.*, **86**, 5478 (1964).

(29) (a) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958); (b) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

(30) J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960); W. M. Jones and R. Damico, *J. Am. Chem. Soc.*, **85**, 2273 (1963).

(31) It has been pointed out that for the case of stereospecific elimination from a haloalkene through an anion,^{5,6} $k_{elim} = k_1k_3(k_2(SH) + k_3)$, where k_1 , k_2 , and k_3 are the rate constants for proton removal from the alkene by base, proton removal from the solvent SH by anion, and halide

(26) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 252–257.

rapidly with deuterated solvents in the presence of base. If it is assumed that the subsequent elimination goes through the ethenide,^{5,29} then the fact that the elimination processes are stereospecific permits us to take E_{act} for elimination as a rough lower limit for ethenide isomerization, $V_i > 30$ kcal/mole.^{5,30} In Table III, our calculated V_i values are probably slightly large by a few kilocalories/mole, but they do seem to be in accord with available data. The fact that α -arylvinyl anions may not be stable has been ascribed to delocalization into the benzene ring,^{22,29a} which our calculations do not take into account.

Apart from compounds with bridgehead nitrogen, no tricoordinated cyclic compounds with nitrogen as the optically active center have been isolated.⁴ But the inversions of some of them, e.g., aziridines¹³ and oxazetidines,³³ have been detected by nmr spectroscopy; ranges of $V_i \approx 5.5$ –15 kcal/mole for these inversions have been established. In the one case in which a rough check is possible, we note that the calculated $V_i \approx 34$ kcal/mole for aziridine is higher—unreasonably so—than the observed range for such compounds.¹³ To obtain $V_i \approx 15$ kcal/mole, $\Delta\alpha$ would have to be decreased from the observed value of 40 to 27°. As for the other heterocyclics, “acceptable” barriers can only be obtained for the following $\Delta\alpha$: 25° for alkylazetidine, 20° for azetidine, and 20° for alkylaziridine.

Qualitative observations as well as kinetic studies provide ample evidence for a wide range ($k = 10^3$ – 10^{-13} sec⁻¹ at 60°) in the steric stability of unsaturated nitrogen compounds, e.g., azo, azoxy, oximes, imines, imido ethers: excellent summaries are available.³⁴ Typical data (k (60°), sec⁻¹; E_a , kcal/mole) are as follows: (CF₃)₂C=NCF(CF₃)₂ (10³; 13); ArCH=NAr (...; 12–18);^{34c} Ar₂C=NAr (10; 17–20); ArN=NC₆H₅ (...; 20–23); Ar₂C=NCH₃ (10⁻⁴; 25–27); C₆H₅NO=NC₆H₅ (...; 23); Ar₂C=NBr (<10⁻⁶; ...); FN=NF(...; 32).^{34d} As for diimine (HN=NH), little is known, although one could easily get the impression that the *syn-anti* conversion is facile.³⁵ (It does seem probable that *syn*-diimine often reduces alkenes stereospecifically *cis*, but this does not tell us about the isomerization barrier.) Two different quantum mechanical calculations give the barrier for *syn-anti* interconversion of diimine as 33 and 9 kcal/mole.^{10c}

In our one test case for the acyclic group, the *trans* to *cis* conversion of difluorodiimine (Table III), we used K (eq 5) from nitrogen trifluoride. Our estimate of V_i turned out to be far too high. In this instance, we have the kind of breakdown that should be anticipated for large $\Delta\alpha$'s, and more generally, for extrapolations from the original C.S. model.

departure from the anion, respectively. In these compounds, the lower limit should be $V_i > E_3$ rather than $V_i > E_{elim}$.

(32) P. Beltrame and G. Cortile, *Atti Accad. Nazl. Lincei, Classe Sci. Fis. Mat. Nat.*, **39**, 475 (1965), give $E_{act} = 41.8$ and 44.8 kcal/mole for the elimination–rearrangement of *cis*- and *trans-p*-methoxyphenyl-1-phenyl-2-chloroethene, respectively, in ethanolic ethoxide.

(33) (a) J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, **61**, 2342 (1965); (b) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(34) (a) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966); (b) D. Y. Curtin and J. W. Hausser, *ibid.*, **83**, 3474 (1961); (c) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, **69**, 1584 (1965); (d) J. Binenboym, A. Burcat, A. Lifshitz, and J. Shamir, *J. Am. Chem. Soc.*, **88**, 5039 (1966).

(35) S. Hunig, *Angew. Chem. Intern. Ed. Engl.*, **4**, 271 (1965); E. J. Blau and B. F. Hochheimer, *J. Chem. Phys.*, **41**, 1174 (1964).

Conclusions

The C.S. model for inversion barriers is obviously far superior to the earlier Kincaid–Henriques approach. In applying the newer model, one should keep in mind the problems we have touched on, namely tunneling, entropy factors, solvation, steric and resonance effects. Nevertheless, in our extensive survey of the C.S. model, we encountered no serious failures, except when the theory itself was approximated and/or pushed too far, e.g., in the examples of Table III. This success may well be lost when many specific molecules are examined. It would appear that the bond parameters and barriers of nitrogen and phosphorus species are most accessible experimentally since these are uncharged. It is on these that the theory can and should be tested.

Our survey has turned up few data on charged species. Clearly, these deserve more attention, the more so since these are often reaction intermediates. We note that one of the most popular means for exploring the properties of carbanions, namely through organometallic compounds, has turned out to be the most difficult to interpret. In this regard, the simplest system in which the configurational identity of a transient can be studied may lie in a mechanistic scheme such as eq 11 where XY_3^\pm may be D, *cis*, *syn*, etc.³⁶

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Appendix

The basic definitions and relations for XY_3 in the C.S. method have been given by Herzberg and will not be repeated here.^{3b,7,8} (A few typographical errors in the necessary equations appear in ref 7.) Our computer programs were written in FORTRAN IV for IBM 7040 or 1620 computers. Our input data (ν_1 , ν_2 , M_X , M_Y , l , α) generated k_1 , k_2 , p , r , s , (S_1/S_2), C_{22} , C_{21} , d_{22} , d_{21} , Δl , V_i , and K . For similar input data, our values of k_1 , k_2 , K , and V_i usually agree closely with those of Weston.⁸ Using the observed ν_1 and ν_2 for ammonia rather than frequencies corrected for anharmonicity, Weston finds $S_1/S_2 = 0.1078$,^{8b} Costain and Sutherland reported $S_1/S_2 = 0.1477$,⁷ our value in this case is 0.0799. It is interesting to note that V_i is rather insensitive to the value of S_1/S_2 . A copy of our computer program is available on request.¹

It should be pointed out that some combinations of input data appear to be incompatible in the C.S. model, and the computer indicates this in some way, e.g., error message, stop, etc. Using the reported ν_1 , ν_2 , and $\alpha = 102.1^\circ$ for nitrogen trifluoride, we obtained k_1 and k_2 , but not V_i . Only when α was raised to 105° did the computer produce V_i .

A few “runs” on the hydronium ion were illustrative of several points. Observed liquid-state frequencies for H_3O^+ and D_3O^+ were employed to obtain an inter-

(36) The stereochemical integrity of radicals was not discussed here. Some qualitative and quantitative data are available: Br₂CHCHBr·, H. Steinmetz and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952); I₂CH·CHI·, R. M. Noyes, R. G. Dickinson, and V. Schomaker, *ibid.*, **67**, 1319 (1945); BrCH=C(CH₃)·, P. S. Skell and R. G. Allen, *ibid.*, **86**, 1559 (1964); C₆H₅(CH₂)C=C(CH₃)·, J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966); L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 2089 (1966); G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88** 4541 (1966).

mediate set of force constants for the hydronium ion. The fitting involved the adjustment of *four* valence-bond force constants. The frequencies corresponding to this adjusted set of force constants were employed for barrier calculations. The bond-stretch and angle-bond force constants calculated using these frequencies

and the simple Herzberg treatment, neglecting interaction terms,³ are nearly identical for H_3O^+ and D_3O^+ but are lower than those obtained using a more complete expression for the potential energy. When the nearly identical force constants are employed to calculate V_i , the isotope effect is very small.

Complexes of *p*-Anisylethylenes. III. The Crystal Structure of the Dichloriodate(I) Salt of the Tetra-*p*-anisylethylene Dication

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Abstract: The crystal structure of the dichloriodate(I) salt of the tetra-*p*-anisylethylene dication was determined from single crystal X-ray diffraction data (film methods, visual estimates of intensity). The ICl_2^- anions exist as nearly linear groups (bond angle = $174.5 \pm 3^\circ$) with I-Cl distances of 2.510 and 2.567 ± 0.006 Å. The anisyl groups attached to the central carbon atoms of the dication are rotated 28.2° from planar orientation because of the *o*-hydrogen interaction. The two three-atom groupings of the central ethylenic carbon atom and its attached phenyl carbon atoms are not planar with each other in the dication, but make an angle of 41° with respect to each other. This apparent reduction of the π -bond order of the central C-C bond in the dication is consistent with the qualitative predictions of simple MO theory.

The X-ray single crystal study of tetraanisylethylene dichloriodate(I) evolved from earlier work in a series concerning complexes of halogens with organic compounds.^{1,2} The physical methods usually used to establish the identity of an organic species, such as freezing point depression, infrared, visible, and ultraviolet spectra, and nmr were used to categorize the dication species and are outlined in a subsequent paper of this series. Although these methods gave very strong evidence for the existence of the tetraanisylethylene (TAE) dication, the evidence of this type for the existence of a dicationic species has frequently been questioned. Therefore, the structure determination was undertaken to give independent evidence for the existence of the dication in the solid state and, at the same time, to determine the detailed geometry of the dication.

Experimental Details

Dark blue-green crystals of the TAE complex were grown slowly by illumination (sunlight) of a carbon tetrachloride solution of tetraanisylethylene and iodine present in a mole ratio of 1:2.³ The identity of the product was confirmed by infrared spectra and chemical analyses. *Anal.* Calcd: C, 42.5; H, 3.3. Found: C, 43.57; H, 3.62. The crystals were quite stable in air.

The cell constants were obtained from two different types of measurements. One set was obtained by a least-squares fit to data obtained from a forward reflection DeWolff-Guinier camera powder diagram ($a = 9.802 \pm 0.007$, $b = 10.937 \pm 0.008$, $c = 16.865 \pm 0.009$ Å, $\beta = 114.54 \pm 0.05^\circ$). The film was calibrated by a simultaneous exposure of a quartz sample. Independent values

of a and b were obtained from back-reflection Weissenberg single crystal diagrams using a least-squares extrapolation method to remove systematic errors ($a = 9.797 \pm 0.003$, $b = 10.962 \pm 0.009$ Å). The averaged values of these monoclinic cell dimensions are $a = 9.798 \pm 0.003$, $b = 10.956 \pm 0.004$, $c = 16.865 \pm 0.009$ Å, $\beta = 114.54 \pm 0.05^\circ$.

The c axis extended in the direction of the needle axis of the crystals. Intensity data were obtained from equinclination Weissenberg diagrams ($hk0$) to ($hk9$) taken with Cu $K\alpha$ radiation, and Buerger precession camera diagrams ($0kl$) to ($5kl$) and ($h0l$) to ($h4l$) with Mo $K\alpha$ radiation. Sufficient repeated visual estimates of the intensities were made so that a standard deviation in the mean intensity was calculated for each reflection. These standard deviations were later used to calculate the weights for the least-squares refinement of structure factors. The intensities were corrected for Lorentz and polarization factors. The specimens used for the intensity data were small enough in diameter so that for one crystal ($\mu R = 0.19$) absorption corrections were neglected, and for a second crystal ($\mu R = 1.20$) absorption corrections were made assuming a cylindrical rod-shaped specimen. A total of 1991 independent reflections were used. Characteristic absences were ($h0l$) with l odd, which indicates that the space group symmetry is either $P2/c$ or Pc . The density, assuming two formula weights of $TAE[ICl_2]_2$ per cell, is 1.612, which agrees well with that measured experimentally by pycnometer, 1.65 g/cm³.

Atom-scattering factors used in the structure factor calculation were taken from the "International Tables for Crystallography."⁴ The Thomas-Fermi values were used for I, while the neutral atom values for Cl, C, O, and H were those based on self-consistent wave functions. Both the real and imaginary dispersion corrections were applied for I, Cl, and O (where applicable) in the final stages of refinement.

Full-matrix, least-squares refinements were carried out using a locally developed program for the IBM 7044. Several types of discrepancy factors were calculated: $R_1 = \sum |\Delta F| / \sum |F_o|$, $R_{1w} = \sum w |\Delta F| / \sum w |F_o|$, and $R_{1h} = [\sum w (\Delta F)^2 / \sum w F_o^2]^{1/2}$.⁵ The weighting scheme used was $w^{1/2} = 1/S_{(F)}$, where $S_{(F)}$ is the standard deviation

(1) R. E. Buckles and W. D. Womer, *J. Am. Chem. Soc.*, **80**, 5055 (1958).

(2) R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. E. Person, *ibid.*, **82**, 2444 (1960).

(3) Further details are given in the following paper of this series.

(4) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 211.

(5) W. C. Hamilton, *Trans. Am. Cryst. Assoc.*, **1**, 17 (1965).