

High Pressure Studies. X. Activation Volumes for Homolysis of Single Bonds¹

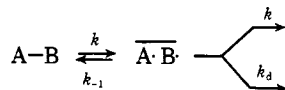
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Abstract: Thermal decomposition of *N*-(1-cyanocyclohexyl)pentamethyleneketanimine (RR'), the ketenimine from azocyanocyclohexane, in chlorobenzene (100°) in the presence of radical scavengers gives pressure dependent observed activation volumes which decrease from *ca.* +13 cc/mol to *ca.* +5 cc/mol with increasing pressure. With no scavenger, ΔV^*_{obsd} is about +5 cc/mol and pressure independent. In the absence of scavengers, the pressure dependence of decomposition of RR' in *tert*-butylbenzene and cumene parallels that in chlorobenzene without and with scavengers, respectively. Products include dicyanobicyclohexyl, cyanocyclohexane, 1-cyanocyclohexene, and products resulting from reaction of cyanocyclohexyl radicals with the solvents cumene and toluene. Quantitative product data as a function of pressure and the kinetic data support the conclusions that observed activation volumes for decomposition of one-bond initiators are substantially larger than the true activation volume for scission of a single chemical bond and that the latter may be *ca.* +5 cc/mol for RR'.

When geminate radicals recombine to form the initiator from which they arose (Scheme I), the kinetic parameters characterizing decomposition of

Scheme I



that initiator are complex quantities. If separative diffusion (k_d) precludes re-formation of AB, the apparent decomposition rate constant (k_{obsd}) depends on the competition between recombination, diffusion, and alternate cage reactions (eq 1).² Similarly, the acti-

$$k_{\text{obsd}} = k_1 \left[\frac{k + k_d}{k_{-1} + k + k_d} \right] \quad (1)$$

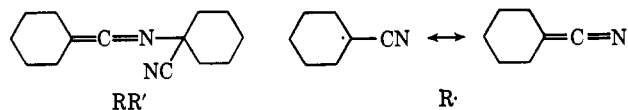
vation parameters obtained from values of k_{obsd} depend on this competition. In particular, the apparent activation volume for loss of initiator (ΔV^*_{obsd}) differs from that for homolytic scission (ΔV^*_1) by the pressure dependence of a quantity related to the cage effect (eq 2).^{1a,3}

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT \partial \ln (1 + k_{-1}/(k + k_d))/\partial P \quad (2)$$

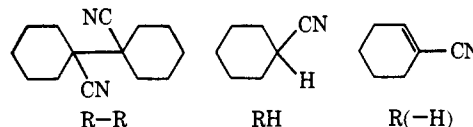
Independent experiments indicate that cage effects are markedly increased by increasing pressure, and we have presumed that this is mainly due to the sensitive inverse dependence of k_d on pressure.^{3,4} These considerations and other experimental studies have led us to propose that values of ΔV^*_{obsd} are generally greater

than values of ΔV^*_1 for systems described by Scheme I.³

We now report the results of a study on a one-bond scission initiator which confirm these proposals. We have investigated the pressure dependence of the decomposition rates of the "ketenimine" (RR') which decomposes to give cyanocyclohexyl radicals (R·)

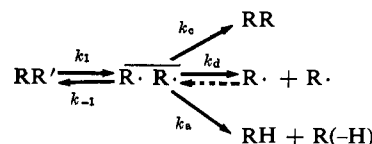


ultimately leading to the stable dinitrile (RR), cyanocyclohexane (RH), and 1-cyanocyclohexene [R(-H)]



(Scheme II).⁵ This system was chosen because the

Scheme II



choice of reaction conditions determines whether or not k_d influences the apparent decomposition rate constant (k_{obsd}). In the presence of radical scavengers, diffused radicals are destroyed and k_{obsd} depends on k_d (eq 3).

$$k_{\text{obsd}} = k_1 \left[\frac{k_c + k_a + k_d}{k_{-1} + k_c + k_a + k_d} \right] \quad (3)$$

In their absence, diffusion is a kinetically "invisible" process and does not appear in the rate expressions (eq 4).^{5,6} A comparison of the decomposition kinetics

(5) (a) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964); (b) C.-H. S. Wu, G. S. Hammond, and J. M. Wright, *ibid.*, **82**, 5386 (1960).

(6) Strictly speaking, Scheme II should distinguish between $R \cdot R \cdot$ formed from RR' and from reencounter of separated radicals. However, such a scheme would be too complex to analyze, and it is likely that there are no major differences between the two types of $R \cdot R \cdot$.

(1) (a) Part IX: R. C. Neuman, Jr., *J. Org. Chem.*, **37**, 495 (1972). (b) Support by the National Science Foundation (GP-8670 and GP-23968) is gratefully acknowledged. (c) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13-17, 1971, Abstract ORGN 141.

(2) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); (b) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970); (c) J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969); (d) H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967).

(3) (a) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **91**, 6024 (1969); (b) R. C. Neuman, Jr., *Intra-Sci. Chem. Rep.*, **3**, 269 (1969); (c) R. C. Neuman, Jr., *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (d) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971); (e) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **36**, 657 (1971); (f) R. C. Neuman, Jr., and G. D. Holmes, *J. Amer. Chem. Soc.*, **93**, 4242 (1971).

(4) The situation is more complex when an inert gas molecule is initially present between the geminate radicals.^{3e}

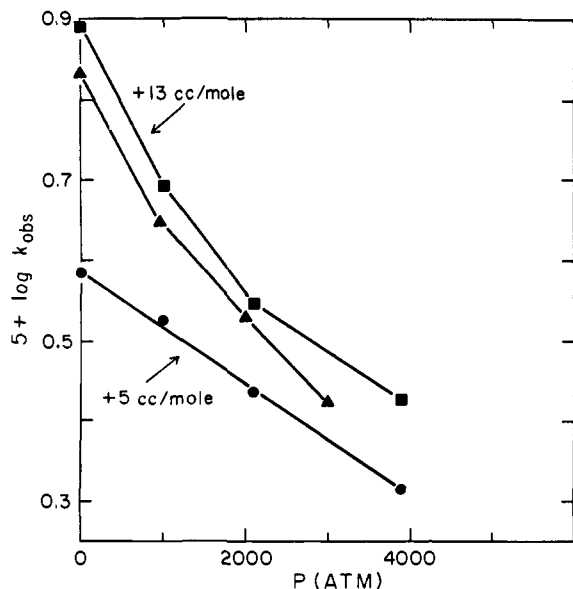


Figure 1. Pressure dependence of decomposition rate for RR' (chlorobenzene, 100°): (■) DBNO scavenger, (▲) DPPH scavenger, (●) no scavenger.

$$k_{\text{obsd}} = k_1 \left[\frac{k_c + k_a}{k_{-1} + k_c + k_a} \right] \quad (4)$$

in these two cases should then provide information about the effect of k_d on values of ΔV^*_{obsd} and the relationship between ΔV^*_{obsd} and ΔV^*_1 in systems of the general type outlined in Scheme I.

Results and Discussion

Apparent rate constants for decomposition of RR' have been determined at 100° in several solvents, both in the presence and absence of scavengers (Table I). In all cases, increasing pressure retards the decom-

Table I. Observed Rate Constants for Decomposition of RR' at Various Pressures (100°)^a

Solvent ^b	Scavenger ^c	P, atm	$k_{\text{obsd}} \times 10^5$, sec ⁻¹
Chlorobenzene	None	1	3.85 ± 0.06
		1000	3.37 ± 0.07
		2050	2.65 ± 0.12
		3900	2.07 ± 0.08
	DPPH	1	6.76 ± 0.13
		2050	3.39 ± 0.09
		3000	2.66 ± 0.12
	DBNO	1	6.50 ± 0.18
		1000	4.25 ± 0.30
		2050	3.33 ± 0.13
Cumene	None	1	3.93 ± 0.05
		2000	2.11 ± 0.02
		3000	1.69 ± 0.07
		3900	1.42 ± 0.05
Toluene	None	1	3.10 ± 0.09
		3000	2.18 ± 0.03
		3900	1.83 ± 0.03
<i>tert</i> -Butylbenzene	None	1	2.39 ± 0.05
		2000	1.68 ± 0.05
		3000	1.36 ± 0.03
		3900	1.22 ± 0.03

^a Determined by ir using absorption at 2020 cm⁻¹. ^b All solutions deoxygenated; RR' concentration ca. 1.5×10^{-2} M. ^c Scavenger concentrations ca. 3×10^{-2} M.

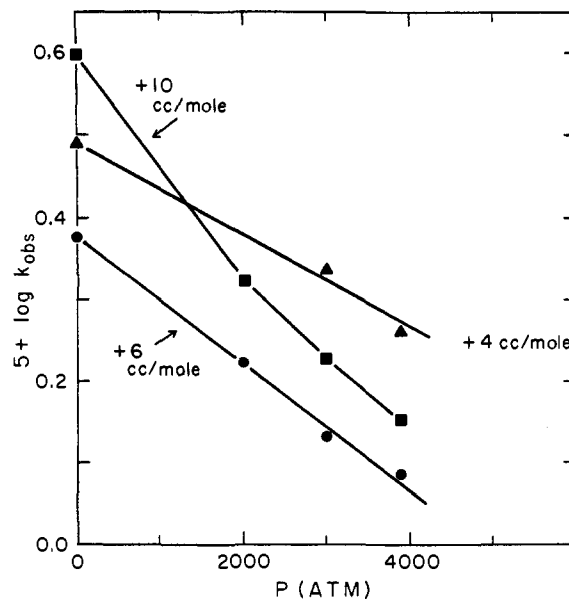


Figure 2. Pressure dependence of decomposition rate for RR' (no scavengers, 100°): (■) cumene, (▲) toluene, (●) *tert*-butylbenzene.

position rates in agreement with results for other free radical initiators³ (Figures 1 and 2).

In the solvent chlorobenzene, the values of k_{obsd} are larger when radical scavengers are present. These scavengers preclude reencounter of separated cyanocyclohexyl radicals and cause separative diffusion to become a destructive pathway for RR'. At atmospheric pressure the data in chlorobenzene (Table I) compare favorably with those of Hammond^{5b} for k_{obsd} at 100°: no scavenger, 4.0×10^{-5} sec⁻¹; DPPH scavenger, 6.6×10^{-5} sec⁻¹.

Apparent activation volumes have been calculated (Table II). Those for chlorobenzene containing

Table II. Apparent Activation Volumes for Decomposition of RR' (100°)^a

Solvent	Scavenger	Pressure range, atm	ΔV^* , cc/mol ^b
Chlorobenzene	DBNO	1-1000	13 ± 3
		1000-2000	7 ± 3
		2000-3900	4 ± 1
	DPPH	1-2000	11 ± 1
		2000-3000	8 ± 2
		<i>c</i>	4.9 ± 0.3
Cumene	None	1-2000	9.5 ± 0.4
		2000-4000	6.4 ± 0.1
	<i>c</i>	5.5 ± 0.2	
<i>tert</i> -Butylbenzene	None	<i>c</i>	5.5 ± 0.2
Toluene	None	<i>c</i>	3.9 ± 0.3

^a See footnotes to Table I. ^b Calculated from data corresponding to "pressure range" (see Figures 1 and 2). ^c Complete pressure range used to obtain ΔV^* (see Figures 1 and 2).

scavengers, and for cumene, have been treated as pressure-dependent quantities, while all of the other values of ΔV^*_{obsd} correspond to the best lines through the experimental points (Figures 1 and 2). It is immediately obvious from the chlorobenzene results that the apparent activation volumes are substantially larger when scavengers are present. This supports the proposal that the pressure dependence of k_d is very influential in determining the magnitude of ΔV^*_{obsd} for one-bond

scission initiators. As pressure increases, the scavenger curves (Figure 1) appear to approach that for the "no scavenger" system. This must indicate that k_d becomes significantly less than $k_c + k_a$ at higher pressures. Since the ratio $k_d/(k_{-1} + k_c + k_a + k_d)$ is ca. 0.3 at atmospheric pressure,^{5a} it is not difficult to imagine that it could approach zero at pressures only slightly larger than those utilized.

While the pressure dependence of k_{obsd} in *tert*-butylbenzene is similar to that obtained in chlorobenzene without scavengers, the curve arising from the data in the structurally similar solvent cumene (isopropylbenzene) looks like those found in chlorobenzene in the presence of scavengers (compare Figures 1 and 2). The reason for this must be that cumene scavenges cyanocyclohexyl radicals (eq 5), and this is supported



by the results of product studies (Table III).⁷

Table III. Product Yields from Decomposition of RR' in Solvents without Added Scavengers (100°)^a

Solvent ^b	P, atm	% yield ^{c,d}					
		RR	RH	R(-H)	RS	Total R	SS
Chlorobenzene	1	77.4	11.0	9.6	<i>e</i>	98.0	<i>e</i>
	3000	55.3	30.8	22.5	<i>e</i>	108.6	<i>e</i>
<i>tert</i> -Butylbenzene	1	88.3	<i>f</i>	(4.5) ^f	<i>e</i>	<i>g</i>	<i>e</i>
	3000	43.9	<i>f</i>	(12.0) ^f	<i>e</i>	<i>g</i>	<i>e</i>
Cumene	1	40.1	43.2	3.0	8.1	94.4	20.3
	3000	42.0	33.5	14.1	<i>e</i>	89.6	13.2
Toluene	1	64.5	19.7	2.9	10.6	97.7	3.2
	3000	52.2	28.7	>3	12.9	96.7	3.2

^a Determined from glpc analyses of totally decomposed samples.

^b All samples deoxygenated. ^c Absolute percentage yields based on initial concentration of RR'. ^d RR = dicyanobicyclohexyl, RH = cyanocyclohexane, and R(-H) = 1-cyanocyclohexene. In cumene: RS presumed to be 1-cumyl-1-cyanocyclohexane; SS = bicumyl. In toluene: RS presumed to be benzylcumyl and perhaps *N*-benzylpentamethyleneketeneimine (see Experimental Section); SS = bibenzyl. ^e Not observed. ^f Completely or partly masked by solvent. ^g Cannot be calculated.

The compounds RR, RH, and R(-H) quantitatively account for RR' in chlorobenzene without scavengers (see Table III and Scheme II). While complete product data could not be obtained using *tert*-butylbenzene, the yields of RR suggest that this system behaves like that in chlorobenzene. On the contrary, in cumene at 1 atm the yield of RR is substantially reduced, that for RH is large, and coupling products involving solvent (S \equiv cumyl) were observed. This supports the incursion of reaction 5 and subsequent bimolecular encounters involving both R· and S·. That the product distribution in cumene at 3000 atm more nearly approximates that at the same pressure in chlorobenzene is expected since separative diffusion becomes increasingly less important as pressure is increased.

(7) (a) A value for $D(\text{R}-\text{H})$ is not available for cyanocyclohexane (RH, eq 5). However, the relative values of E_a for decomposition of azocyanocyclohexane (35.4 kcal/mol)^{7b} and azocumene^{7c} (28.4 kcal/mol) suggest that reaction 5 is exothermic. The product data also indicate that toluene acts as an inefficient scavenger for R· (Table III), and this is consistent with the value of E_a for 1,1'-diphenylazomethane (35.0 kcal/mol).^{7b} (b) C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., 1966, Chapter 4; (c) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

The formation of products containing benzyl radicals indicates that toluene also scavenges R· (Table III). However, it appears to be an inefficient scavenger since (1) the product distribution (1 atm) is intermediate to those in chlorobenzene and cumene and (2) the atmospheric pressure value of k_{obsd} lies between the values found using cumene and *tert*-butylbenzene.^{7,8} The "normal" shape of the toluene curve (Figure 2) is probably an artifact arising because toluene does not completely preclude return of separated cyanocyclohexyl radicals.

The apparent independence on k_d of ΔV^*_{obsd} for decomposition of RR' in chlorobenzene in the absence of scavengers (+5 cc/mol) suggests that it may be a close approximation to ΔV^*_1 .^{3,4} For this to be true the equality shown in eq 6 would be necessary.⁹ Since

$$[k_{-1}/(k_c + k_a)]_{1 \text{ atm}} = [k_{-1}/(k_c + k_a)]_{3000 \text{ atm}} \quad (6)$$

the product data (Table III) give values of 0.28 and 1.11, respectively, for k_a/k_c at 1 and 3000 atm (chlorobenzene),¹⁰ eq 6 is satisfied if k_{-1}/k_c is about 1.7 times larger at 3000 atm than at 1 atm. While this cannot be experimentally verified, it seems possible that increasing pressure could decrease the ability of geminate radicals formed from RR' to achieve an equilibrium orientation distribution relative to each other prior to cage reactions.¹¹ This could lead to a memory effect where recombination of nondiffused radicals would increasingly favor RR' formation over that of RR at higher pressures. Since diffusion is substantially reduced at the higher pressures, this effect would be enhanced.

Experimental Section

Syntheses. **1,1'-Azocyanocyclohexane** was synthesized by bromine oxidation of the hydrazo precursor following published procedures;^{5b} yield 93%; mp 113–115° dec (lit.^{5b} 113–114° dec); λ_{max} (95% ethyl alcohol) 350 m μ (ϵ 18.2) (lit.^{5b} 350 m μ (ϵ 17.9)). ***N*-(1-Cyanocyclohexyl)pentamethyleneketeneimine (RR')** was isolated from thermal decomposition of 1,1'-azocyanocyclohexane in refluxing heptane (N_2 atmosphere) according to established procedures^{5b} and purified by repeated sublimation: mp 67–69° (lit.^{5b} 68–69°); ir ϵ at 2020 cm⁻¹ in carbon tetrachloride, 540 M⁻¹ cm⁻¹ (lit.^{5b} 456 M⁻¹ cm⁻¹). **1,1'-Dicyanobicyclohexyl (RR)** was isolated from the reaction used to prepare RR', mp 218–220° (lit.^{5b} 224–226°). **Cyanocyclohexane** was synthesized from cyclohexanecarboxylic acid *via* the amide utilizing standard procedures;¹² bp 81.5–82.0° (37 mm); ir 2230 cm⁻¹; nmr broad multiplet τ 7.82–9.00 (area 10), broad singlet 7.16–7.76 (area 1). *Anal.* Calcd for C₆H₁₁N: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.72, 76.82; H, 10.15, 10.11; N, 12.35, 12.32. **Di-*tert*-butyl nitroxide (DBNO)** was prepared from *tert*-nitrobutane;¹³ yield 18%; bp

(8) Since toluene, isopropylbenzene, and *tert*-butylbenzene are similar solvents, we feel that the differences in k_{obsd} mainly reside in the *apparent* relative importance of k_d (see eq 3 and Scheme II).

(9) In the absence of scavengers, ΔV^*_{obsd} equals $\Delta V^*_1 + RT \ln [1 + k_{-1}/(k_c + k_a)]/\partial P$. The equality shown in eq 6 follows if the latter differential term is equal to zero.

(10) The quantity k_a/k_c equals the product ratio 2(RH)/(RR).

(11) The pressure dependence of k_a/k_c may also reflect this effect. Professor J. M. McBride has found that the relative importance of disproportionation from geminate cyanoisopropyl radicals generated from AIBN is substantially different in liquid and solid phases. He attributes this to a medium effect on "rotational diffusion" in the geminate aggregate: J. M. McBride, *J. Amer. Chem. Soc.*, **93**, 6302 (1971).

(12) See (a) R. E. Kent and S. M. McElvain, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 490; (b) J. A. Krynitsky and H. W. Carhart, *ibid.*, Collect. Vol. IV, 1963, p 436.

(13) (a) N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Amer. Chem. Soc.*, **78**, 4003 (1956); (b) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

64–65° (14.5 mm) (lit.^{13b} 60° (11 mm)); λ (hexane) 465 μ (ϵ 9.0), 238 μ (ϵ 2.25 \times 10³) (lit.^{13b} 465 μ (ϵ 8.9), 238 μ (ϵ 2.14 \times 10³)).

Commercial Materials. Diphenylpicrylhydrazyl (DPPH) was purchased from Aldrich Chemical Co. and recrystallized prior to its use. Chlorobenzene (MCB) was treated with sulfuric acid, and aqueous sodium bicarbonate, washed, dried, and distilled, bp 129.8–129.9°. Cumene (MCB) was treated with sulfuric acid and aqueous sodium bicarbonate, washed, dried, and distilled under an atmosphere of nitrogen, bp 145.5–147.0°. It was stored and opened only under atmospheres of argon or nitrogen. Toluene (Mallinckrodt Reagent Grade) was acid-washed, dried, and distilled, bp 107.1–107.5°. *tert*-Butylbenzene (MCB Reagent Grade) was used without further purification. Analysis by glpc indicated the presence of only a trace of high-boiling impurities.

Kinetic Studies. Solutions 1.5 \times 10⁻² M in RR' were prepared in the various solvents. Those containing scavengers were prepared to be ca. 3 \times 10⁻² M in DBNO or DPPH. Solvents were purged with argon for 30 min, and solutions were prepared and stored in a glove bag under a positive pressure of argon. Solutions were purged with argon subsequent to their preparation and used shortly thereafter. All manipulations were carried out under an inert atmosphere. Individual kinetic samples in capped Teflon ampoules were decomposed under high pressure following standard procedures.³ Atmospheric pressure samples were decomposed in degassed glass ampoules. Samples for each run were analyzed for intensity of the infrared absorption band at 2020 cm⁻¹ using either

a PE 621 or PE 21 infrared spectrometer. Control experiments indicated that both instruments gave comparable kinetic results within experimental error.

Product Studies. Solutions containing RR' (ca. 1.5 \times 10⁻² M) and an internal standard were prepared in the various solvents as described above. These were completely decomposed and analyzed by glpc using a temperature programmed F & M Model 700 thermal conductivity gas chromatograph equipped with a matched pair of 6 ft \times 1/8 in. 10% UC-W98 columns. Product identities were deduced from retention times (*vide infra*), and yields were determined from peak areas measured using a Disc integrator. Under conditions used in these studies authentic samples gave the following retention times: RR (27.0 min), RH (13.4 min), bicumyl (28.5 min), and bibenzyl (22.6 min).¹⁴ A peak detected at 14.6 min in all reaction mixtures was assumed to be R(-H). In cumene, a product presumed to be RS was observed at 29.0 min; in toluene, peaks at ca. 25 min are also presumed to be RS. Accurate area ratio-concentration ratio data were determined for RR and RH. A value for R(-H) was assumed to be the same as for RH; values for SS and RS were assumed to be the same as those for RR.¹⁵

(14) Bicumyl and bibenzyl were available from earlier studies.³

(15) Complete experimental details can be found in the Ph.D. dissertation of M. J. Amrich, University of California, Riverside, Calif., 1971.

Boiling Points and Structure of Chloro- and Methyl-Substituted Ethylene Carbonates. Steric Hindrance to Dipolar Interaction

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Abstract: Data which show the degree to which five-membered cyclic compounds boil higher than their acyclic analogs are presented. This effect is due mainly to the increase in dipole moment of the cyclic compounds as compared to the acyclic analogs. Substitution of chlorine and methyl groups in ethylene carbonate causes a decrease in boiling point. Part of this decrease is due to steric hindrance to dipolar interaction. By empirical calculations based on qualitative assumptions, the steric effects of methyl groups and chloro groups on the boiling point of ethylene carbonate are shown to be about the same.

The main objectives of this article are to point out the unusually high boiling points of certain oxygen five-membered heterocyclic compounds, as compared to those of the corresponding acyclic analogs, and to show how polar and steric factors affect the boiling points of substitution products of ethylene carbonate, a representative five-membered heterocycle.

The interest in this area arose from the fact that both chloroethylene carbonate (2), bp 212°, and *rac*-dichloroethylene carbonate (3), bp 178°, boil² appreciably lower than ethylene carbonate (1), bp 248°.³ These results were surprising because normally the replacement of a hydrogen on carbon by chlorine leads to an appreciable increase in boiling point.⁴

(1) The data presented in this paper were taken from the M.S. thesis of R. A. M., Ohio State University, 1964.

(2) All boiling points cited in this article are in °C at atmospheric pressure, 750 \pm 10 mm, and are taken from the "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967–1968, unless otherwise noted.

(3) M. S. Newman and R. Addor, *J. Amer. Chem. Soc.*, **77**, 3789 (1955).

(4) For example, ethyl acetate boils at 77°, whereas ethyl chloroacetate boils at 144°, α -chloroethyl acetate at 121.5°, and β -chloroethyl acetate at 145°.

Before discussing the lowering of the boiling point of 1 by substitution of chlorines, it is of interest to know why 1 has such a high boiling point and to compare the boiling points of a number of five-atom cyclic compounds with those of the corresponding acyclic analogs (see Table I).

The boiling point of a liquid has been defined by eq 1,⁵ where T = boiling point in degrees absolute,

$$T = \Delta H_{\text{vap}} / \Delta S_{\text{vap}} \quad (1)$$

ΔH_{vap} = heat of vaporization in kcal/mol at the boiling point, and ΔS_{vap} = entropy of vaporization in kcal/(mol deg) at the boiling point.

ΔH_{vap} represents the intermolecular forces which must be overcome before vaporization can occur. These forces arise from van der Waals attractions (dispersion forces), dipole-dipole interaction, and hydrogen bonding. In this discussion hydrogen bonding is ignored because hydrogen bonding is not thought to be appreciably involved in the compounds under

(5) W. J. Moore, "Physical Chemistry," Prentice-Hall, 3rd ed, Englewood Cliffs, N. J., 1962, p 80.