

$n = (n_1 n_2)^{1/2}$, which were successful in describing hydrocarbon mixtures.⁷ The subscripts in these formulas indicate the parameters for the pure components.

The calculated value of B_{12} , $-1295 \text{ cm}^3/\text{mol}$, is in fair agreement with the value determined from our measurements, $-1238 \text{ cm}^3/\text{mol}$. As a further check of the reliability for these systems of the corresponding states approach we calculate $-1052 \text{ cm}^3/\text{mol}$ for the B_{12} for benzene-cyclohexane at 75° . This agrees favorably with the literature values -1075 ± 9^{15} and $-1010 \text{ cm}^3/\text{mol}$.¹⁶ The success of these calculations indicates that the interaction virial coefficients obtained from eq 1 are almost certainly reliable to $\pm 60 \text{ cm}^3/\text{mol}$.

Calculated and observed interaction virial coefficients for B-HFB are compared in Table III. The observed B_{12} values are from 450 to $1200 \text{ cm}^3/\text{mol}$ larger in magnitude than those obtained from the corresponding states calculations. This is precisely what would be expected if a complex were formed in the vapor mixture. The equilibrium constants given in Table III are obtained from eq 2 when the calculated virial coefficients are assumed to represent B_{12}^p . A plot of $\log K_p$ vs. $1/T$ is linear, and from its slope a value of $-5.6 \pm 1.5 \text{ kcal/mol}$ is obtained for ΔH_{form} , the heat of formation of the complex.

Recently, Gaw and Swinton² analyzed their measurements of the excess Gibbs free energy, g^e , of B-HFB liquid mixtures under the assumption that a B-HFB complex exists. From their data they obtain equilibrium constants which are roughly an order of magnitude larger than those reported here and they find a ΔH_{form} of -2.3 kcal/mol .

Like the procedure for virial coefficients described here, their analysis requires that the free energy be separated into a physical and a chemical contribution. They have assumed that the g^e for the cyclohexane-HFB system provides a reasonable estimate of the physical g^e for B-HFB. At 50° for an equimolar B-HFB mixture g^e is -50 J/mol and the physical g^e is 755 J/mol . (The value -50 J/mol differs from that reported in ref 2. Gaw and Swinton assumed in the treatment of their data that $\epsilon = 0$. The g^e cited here has been recalculated from their vapor pressure data using the virial coefficients reported here.) Thus, the chemical contribution to the excess free energy, -805 J/mol , is almost completely determined by the choice made for the physical part.

Because of the uncertainties and approximations

Table III: Calculated and Observed B_{12} for B-HFB

$T, ^\circ\text{C}$	$B_{12} \text{ obsd.}, \text{ cm}^3/\text{mol}$	$B_{12} \text{ calcd.}, \text{ cm}^3/\text{mol}$	$\Delta B_{12}, \text{ cm}^3/\text{mol}$	$K_p, \text{ atm}^{-1}$
50	-2613	-1514	-1099	0.083
75	-1837	-1223	-614	0.043
100	-1406 ^a	-1011	-395	0.026

^a Average of two values.

made in the treatments of the free energy and the virial coefficient data, it cannot be stated that there is a significant difference between the gas and liquid phase results. However, to bring the values for the equilibrium constants into agreement, it would be necessary either to cut the physical contribution to g^e or radically reduce B_{12}^p . A change of $400 \text{ cm}^3/\text{mol}$ in B_{12}^p produces only a 35% increase in K_p . It is very unlikely that either of the estimates of physical contributions could be so much in error.

Acknowledgment. We thank Dr. D. R. Douslin for making the critical constants of hexafluorobenzene available to us before publication.

(15) F. G. Waelbroeck, *J. Chem. Phys.*, **23**, 749 (1955).

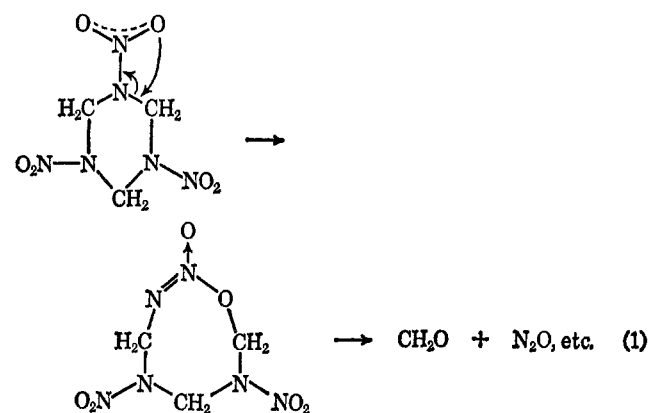
(16) Obtained by extrapolation of the data of G. A. Bottomley and I. H. Coopes, *Nature*, **193**, 268 (1962).

The Thermal Decomposition Kinetics of Hexahydro-1,3,5-trinitro-s-triazine above the Melting Point: Evidence for Both a Gas and Liquid Phase Decomposition

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Until a recent revival of interest, the most thorough study of the thermal decomposition of hexahydro-1,3,5-trinitro-s-triazine (RDX) was that of Robertson, who determined the kinetics above the melting point from pressure-time curves of the evolved gases.¹ From the nature of the gaseous products formed, especially the large amounts of N_2O and CH_2O , it was suggested that the primary step involved transfer of an oxygen atom from the nitramino group to a neighboring carbon followed by elimination of CH_2O and N_2O , possibly through an oxadiazole intermediate (eq 1). Further



(1) A. J. B. Robertson, *Trans. Faraday Soc.*, **45**, 85 (1949).

evidence for a mechanism of this type, *i.e.*, not involving N-N bond rupture, has been obtained by Suryanarayana, Graybush, and Autera from studies on isotopically labeled octahydro-1,3,5,7-tetranitro-*s*-tetrazine (HMX)² and to a lesser extent RDX.³ In the case of decomposition of RDX below the melting point, Cosgrove and Owen have recently presented evidence that the major part of the reaction actually occurs in the gas phase and not in the solid.⁴ NO₂ was not reported as a product in any of these investigations.

Presently, a detailed study of the decomposition kinetics of RDX above its melting point has been undertaken in this laboratory principally to extend the earlier results of Robertson, especially with regard to the question of inter- *vs.* intramolecular mechanisms, and to provide a basis for future work on the decomposition of mixtures of nitro-containing compounds. As secondary reactions might be expected to contribute to the total pressure rise in a molecule as complex as RDX, the rate of decomposition was followed by direct determination of the RDX. The results obtained, thus far, indicate that at temperatures above the melting point decomposition occurs simultaneously in the gas phase and in the liquid phase, and further that the mechanism of the gas phase decomposition is not the same as that for the liquid, the former almost certainly involving rupture of the nitramino N-N bond and formation of NO₂, whereas the latter does not.

Experimental Section

Material. The purified RDX used as starting material was kindly supplied to us by Dr. B. Suryanarayana of the Explosives Laboratory, Picatinny Arsenal, Dover, N. J. This material was obtained from technical grade RDX (Holston Defense Corp.) by the following procedure. Most of the HMX impurity is removed by recrystallizing the technical grade RDX from γ -butyrolactone. This material is then successively recrystallized from 75:25, 50:50, and 50:50 H₂O-acetone solutions. The material obtained after the fourth recrystallization has a melting point of 204.5–205° dec. No impurity peaks could be detected on a chromatogram of an acetone solution of this material at maximum sensitivity (0.1-mV full scale) using thermal conductivity detection. Impurity levels of 0.02% have been detected in technical grade RDX under the same conditions. From the high melting point and the absence of chromatographic impurities it is estimated that the purity of the starting materials is greater than 99.9%.

Kinetic Procedure. The reactors employed were Pyrex glass vessels, 26, 100, and 300 ml in volume and equipped with two arms terminating in ball joints. One arm contained a break-seal which could be ruptured for analysis of the product gases. The RDX was charged into the reactor through the second arm, which was then sealed off under vacuum (or in a few instances under pressure of inert gas).

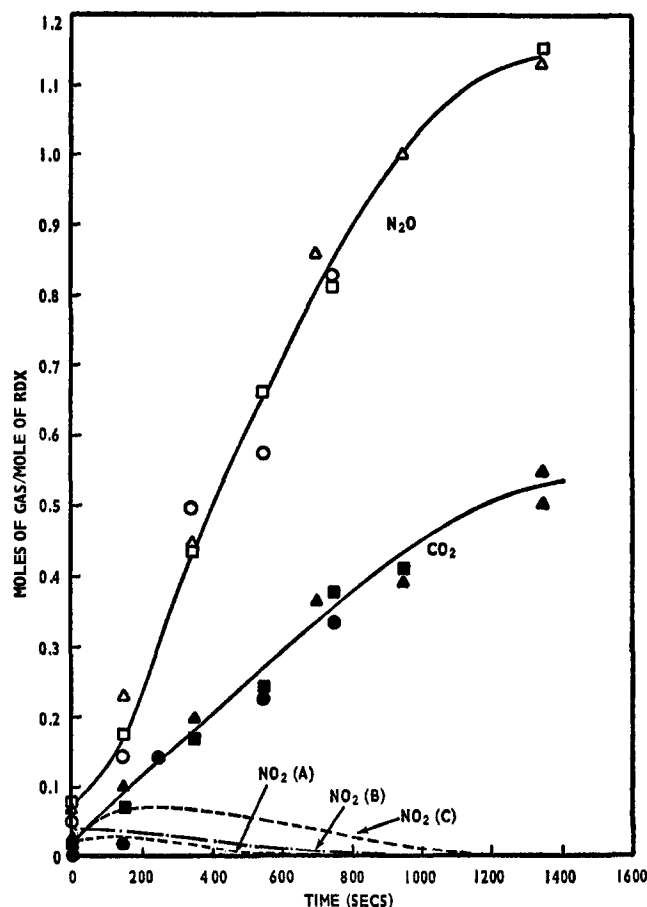


Figure 1. Concentration-time profiles of N₂O, CO₂, and NO₂ for three initial weights of RDX. N₂O and CO₂ curves: ○ and ●, 12.5 mg; △ and ▲, 26 mg; □ and ■, 40 mg. NO₂ curves: A, 12.5 mg; B, 26 mg; C, 40 mg. Reactor volume, 26 ml. (See Figure 3 for data points of NO₂.)

The following procedure was used in making a run. Six to eight of the charged reactors were immersed in a temperature-controlled, fluidized sand bath up to a level such that the entire volume of the reactor available to the RDX or its gaseous decomposition products was at the bath temperature. A 3-min heat-up time was allowed for obtaining thermal equilibrium since it was found that for several 40-mg samples (the largest initial weight employed) that 2–2.5 min was required for complete liquefaction at 207°. One of the reactors was withdrawn after this 3-min equilibration period, and the reaction was quenched by immersion in ice-water to establish the appropriate levels of RDX and decomposition products at this kinetic time zero. The remaining reactors were removed from the bath and quenched at appropriate time intervals. All time intervals given are referred to the kinetic time zero.

Quantitative analysis of the products was carried out by gas chromatography under the following condi-

(2) B. Suryanarayana, R. J. Graybush, and J. R. Autera, *Chem. Ind. (London)*, 2177 (1967).

(3) B. Suryanarayana, private communication.

(4) J. D. Cosgrove and A. J. Owen, *Chem. Commun.*, 286 (1968).

tions: N_2O , CO_2 , and HCN on a 10-ft Porapak Q column (Dow Chemical Co.) at 70° ; N_2 , CO , and NO on a 10-ft Linde 13X molecular sieve column at 25° ; H_2O and CH_2O on a 10-ft polyoxyethylene glycol searate column at 95° . These analyses were confirmed and in some cases extended by infrared, ultraviolet, and mass spectroscopic measurements. The amount of NO_2 generated during the decomposition could not be measured chromatographically under the conditions employed for the other gases. Its level at any time was determined from its ultraviolet absorbance spectrum using the band at $413 \text{ m}\mu$, which was found not to be pressure broadened. (The change in the absorbance of the infrared bands of NO_2 gives only a semiquantitative measure of the amount present at these bands are quite sensitive to pressure broadening effects.) The uv cell employed consisted of two quartz windows sealed to a cylindrical glass section, 12.5 cm in length \times 1.9 cm i.d., and fitted with a Fischer-Porter valve. All of the spectroscopic measurements were carried out on a Cary Model 14 recording spectrophotometer.

The amount of RDX undecomposed was directly determined by the gas chromatographic procedure of Rowe,⁵ after dissolving the nonvolatile reactor contents in dimethyl sulfoxide containing 1% dipentyl phthalate as an internal standard.

Results and Discussion

In the course of these experiments a small amount of NO_2 was consistently observed both visually and instrumentally, as a product of the decomposition. Its growth curve at five temperatures in the range 207 – 227°

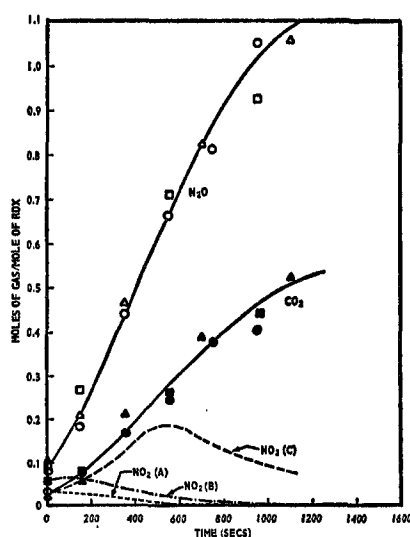


Figure 2. Concentration-time profiles of N_2O , CO_2 , and NO_2 for three reactor volumes. N_2O and CO_2 curves: \circ and \bullet , 26 ml; \triangle and \blacktriangle , 100 ml; \square and \blacksquare , 300 ml. NO_2 curves: A, 26 ml; B, 100 ml; C, 300 ml. Initial weight of RDX, 40 mg. (See Figure 3 for data points of NO_2 .)

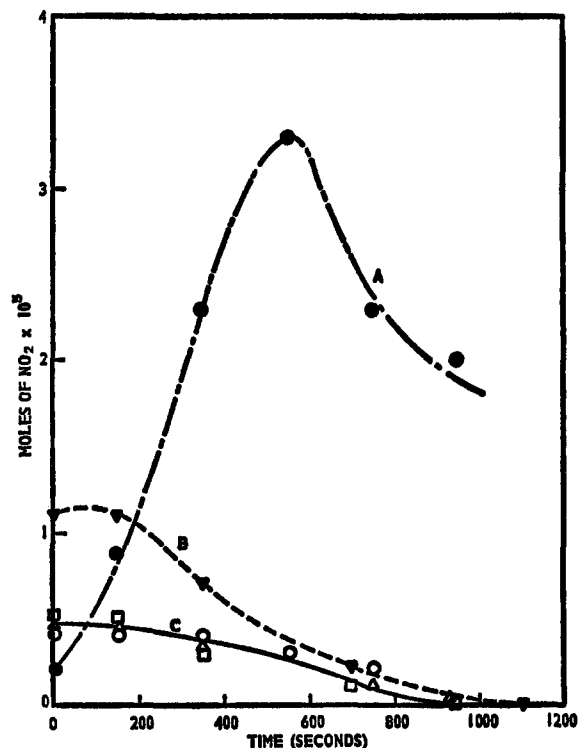


Figure 3. Concentration-time profiles of NO_2 for various initial weights of RDX and reactor volumes. Initial weights and volumes: A, 300 ml, 40 mg; B, 100 ml, 40 mg; C, 26 ml, 12.5 mg (\circ), 26 mg (\triangle), 41.0 mg (\square).

passes through a maximum relatively early in the decomposition and then falls off rapidly, principally because of secondary reactions. The other gaseous products include N_2O , NO , CH_2O , CO , CO_2 , H_2O , and HCN . As reported by Robertson, the rate of decomposition of the RDX was found to follow first-order kinetics over the temperature range investigated. Figures 1, 2, and 3 summarize the principal evidence for concurrent gas and liquid phase decompositions. Figure 1 shows the amounts of N_2O , CO_2 , and NO_2 produced per initial mole of RDX at 212° for varying initial weights of RDX in constant volume reactors, whereas Figure 2 presents the concentration-time profiles of the same three products for a constant initial weight of RDX in reactors of different volume. Figure 3 illustrates the data for NO_2 used in Figures 1 and 2 on an absolute basis and on an expanded ordinate scale. The profiles of the other gaseous products are not shown for the sake of clarity, but all follow the same general pattern as evidenced by N_2O and CO_2 . Table I lists the rate constants and other kinetic data for these same runs.

The results shown in these figures along with the rate data of Table I can be rationalized only if the NO_2 arises from a gas phase decomposition whereas all other gaseous products found thus far are produced in a

(5) M. L. Rowe, *J. Gas Chromatography*, **4**, 531 (1967).

Table I: Kinetic Data for the Decomposition of RDX at 212°

Initial weight ^a of RDX, mg	Reaction ^a volume, ml	Rate constant, sec ⁻¹ × 10 ³	RDX ^b in gas phase, %
40.0	300	2.2 ± 0.2	0.3
40.0	100	2.1 ± 0.1	1.2
40.0	26	1.9 ± 0.2	3.6
26.0	26	1.7 ± 0.2	0.5
12.5	26	2.0 ± 0.1	1.0

^a Reactors sealed under vacuum. ^b Calculated from vapor pressure data of ref 6; see text.

liquid phase reaction. Because the amount of RDX in the gas phase will be a function of the vapor pressure at that temperature, on a per initial mole basis products arising from a liquid phase reaction should be independent of both initial weight and reactor volume. By contrast the absolute amount of product generated by a gas phase process should be independent of the initial weight and increase proportionately with reactor volume. N₂O and CO₂ clearly follow the former pattern and NO₂ the latter. The rate constants of Table I calculated by changes in the total amount of RDX are seen to be virtually unchanged within experimental error under the various conditions of initial weight and reactor volume. This invariance of the rate constant indicates that the gas phase decomposition represents only a relatively small fraction of the total degradation process. The last column in Table I shows the percentage of RDX initially present in the gas phase at 212° for the various conditions based on extrapolation of the vapor pressure data of Edwards for solid RDX.⁶ This calculation leads to a value of about 0.6 mm at 212°. Although this figure may be an underestimation and certainly not of sufficient accuracy to allow more than a crude estimate of the gas phase reaction rate, it does indicate to a fair approximation that the fraction of RDX in the gas phase will be small except in very large volume reactors. Using the data from the 300-ml reactor run, the only one in which the initial rate of NO₂ formation can be estimated, a rough value of 8×10^{-3} sec⁻¹ is calculated for an assumed first-order reaction. This value is seen to be of the same order of magnitude as those based on the disappearance of RDX and indicates that the values of the rate constant shown in Table I for the small reactors are to a good approximation those for the liquid phase decomposition. Although not statistically significant, the small increase in rate constant with volume shown in Table I may be real, reflecting the increasing participation of the gas phase reaction in the total decomposition under these conditions.

As is apparent from the decay portion of the NO₂ profiles, this product undergoes further reaction. Be-

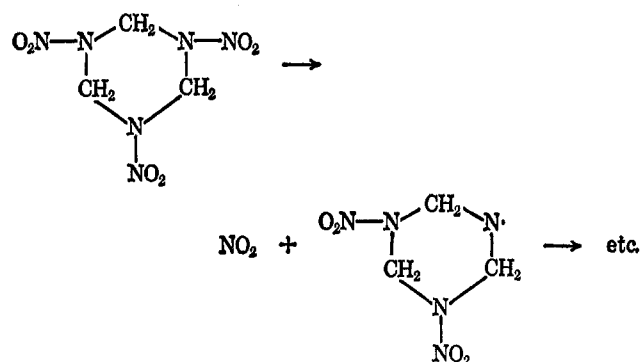
cause the nature of this secondary reaction (or reactions) is unknown, and because the vapor pressure of RDX probably decreases during the course of reaction due to the formation of nonvolatile products, the direct dependence of the total amount of NO₂ produced on the reactor volume is not easily demonstrated. However, the maxima in the NO₂ profiles should be more-or-less directly related to the total amount produced. Comparison of the peak NO₂ values in Figure 3 for the three reactor volumes indicates that to a good approximation this is true.

The appearance of NO₂ as a product in these experiments is in contradistinction to the results of two of the studies cited above.^{1,2} In Cosgrove and Owen's work, the identities of all of the gaseous products were not reported.⁴ The differences in results are probably ascribable to the different experimental techniques employed. In the previous investigations, with the exception of Cosgrove and Owen's work, a portion of the apparatus is heated, whereas another portion is closer to room temperature, allowing the vaporizing RDX to condense in the cold zone before decomposition. In this work gaseous RDX is present in the uniformly heated reactors at its vapor pressure; hence, gas phase decomposition has the opportunity to occur. It should also be noted that in the previous studies, again with the exception of Cosgrove and Owen's work, a small pressure of inert gas was added to repress the vaporization, whereas for all of the runs shown in the figures the reactors were initially sealed under vacuum. A single run was made in these studies under inert gas pressure (400 mm He at 25°) in the 26-ml reactors to determine the effect of suppression of the vaporization. The data for this run showed that the observed rate of disappearance of RDX was essentially unaffected, and the total amount of NO₂ produced in the entire course of the decomposition was approximately the same as for the runs under initial vacuum conditions. In this case, however, the peak in the NO₂ profile did appear at a later time than that shown in Figure 1, presumably reflecting the initial suppression of the vaporization process.

We have found no evidence in the course of these studies for any other gaseous products besides NO₂ which show the same dependence on reactor volume and initial weight. However, the absolute amount of such species would certainly be small at any time and almost certainly degrade rapidly to the ultimate decomposition products. Quite probably, such products would in many instances be the same as those generated in the liquid phase reaction. Nonetheless, despite the lack of supporting chemical evidence, the rapid initial production of NO₂ suggests that the first step in the gas phase decomposition mechanism is the homolytic

(6) G. Edwards, *Trans. Faraday Soc.*, **49**, 152 (1953).

rupture of the nitramino N-N bond in a unimolecular process.



Although it would be of some interest to extend the product distribution measurements of Figures 1, 2, and 3 to higher initial weights, larger reactor volumes, and other temperatures above the melting point of RDX, it is unlikely that significantly more information can be obtained with our present techniques since their utility is limited by a number of practical difficulties. It has been found that with initial weights larger than 40 mg, "fume offs" and even explosions frequently occur, particularly at higher temperatures. As would be expected, at higher temperatures the peak in the NO_2 profile is found to occur even earlier in the decomposition. Also, our present experimental procedure does not allow for reactor volumes significantly larger than 300 ml. It is interesting to note, however, that with small enough initial weights and very large reactors (10-mg initial weight in a volume of 3000 ml), it should be possible, in principle, to isolate the gas phase decomposition. Further work on the decomposition below the melting point may also be relevant in this regard.

It has already been noted that the essential agreement of the rate constants for different reactor volumes and initial weights would appear to indicate that these values are to a good approximation those for the liquid phase decomposition, the gas phase decomposition making a negligible contribution to the over-all rate under most conditions. In fact, with the exception of NO_2 , the rate data and gaseous product distribution were found to be in excellent agreement with the results of Robertson.¹ From our first-order rate constants at five temperatures using the 26-ml reactors the activation energy and frequency factor are calculated to be 48.7 kcal/mol and $1.7 \times 10^{19} \text{ sec}^{-1}$, respectively; Robertson reported values of 47.5 kcal/mol and $3.2 \times 10^{18} \text{ sec}^{-1}$. The details of the liquid phase decomposition will be taken up in a later communication.

Acknowledgement. This work was supported by Picatinny Arsenal, U. S. Army Munitions Command.

The Radiation-Induced Isomerization of Cyclohexane on Silica-Alumina

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(Received November 11, 1968)

Acid sites of silica-aluminas catalyze the dealkylation of isopropylbenzene² and such reactions of alkanes as cracking,^{3,4} isomerization,³ and exchange of H atoms with the catalyst.⁴ Presumably such acid sites function by formation of carbonium ions from the adsorbate. Certain centers produced in silica-alumina and silica gels by γ irradiation cause dealkylation of isopropylbenzene at room temperature as shown in studies of (1) the γ irradiation of isopropylbenzene adsorbed on silica-alumina⁵ and silica gels⁶ and (2) the reaction of isopropylbenzene on γ -irradiated silica-alumina^{5a,7} and silica⁶ gels. Such studies indicate that an appreciable portion of the dealkylation on a γ -irradiated silica-alumina is associated with the bleaching of radiation-induced visible color centers, which have been identified as positive holes trapped at certain of the aluminum atoms present substitutionally in the silica matrix.⁸ Thus, the Al positive-hole center promotes a reaction that is catalyzed by acid sites. Addition of cyclohexane to a γ -irradiated silica-alumina also removes the characteristic visible color and esr signal of the Al positive-hole center.⁸ Consequently, it is of interest to see whether γ -irradiated silica-alumina causes the acid-catalyzed isomerization of cyclohexane to methylcyclopentane (MCP).

Experimental Section

Phillips research grade cyclohexane was used. The silica-alumina (10 wt % alumina and 400 m²/g of surface area) has been used in previous work.^{5,7} Experimental procedures were essentially the same as in the work with isopropylbenzene and silica gel.⁶ The solid was crushed with a Diamonite mortar and pestle and passed through sieves of 20 and 40 mesh. After 19 hr at 500° in air, solid was weighed into a 13-mm

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-632.

(2) A. E. Hirschler, *J. Catal.*, **2**, 428 (1963); D. Barthomeuf, *Compt. Rend.*, **259**, 3520 (1964).

(3) S. G. Hindin, A. G. Oblad, and G. A. Mills, *J. Amer. Chem. Soc.*, **77**, 535 (1955).

(4) S. G. Hindin, G. A. Mills, and A. G. Oblad, *ibid.*, **73**, 278 (1951); **77**, 538 (1955).

(5) (a) R. R. Hentz, *J. Phys. Chem.*, **68**, 2889 (1964); (b) R. R. Hentz, *ibid.*, **66**, 1625 (1962).

(6) E. A. Rojo and R. R. Hentz, *ibid.*, **70**, 2919 (1966).

(7) Cf. R. R. Hentz, L. M. Perkey, and R. H. Williams, *ibid.*, **70**, 731 (1966), which includes references to all other papers in this series.

(8) R. R. Hentz and D. K. Wickenden, *ibid.*, in press.