Photolysis of Tetrahydrofuran in the Gas Phase[1]

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Abstract: The photolysis of tetrahydrofuran was carried out in the pressure range 10–165 mm and at temperatures 30–120°. The main products detected were carbon monoxide, hydrogen, methane, ethane, ethylene, propylene, cyclopropane, propane, and formaldehyde. These products were postulated to have been formed *via* the intermediate formation of a diradical which was generated as a result of the rupture of a relatively weak carbon–oxygen bond in tetrahydrofuran. The product distribution as a function of pressure indicated the existence of vibrationally excited cyclopropane with an average lifetime of 10^{-7} sec. The RRMK theory of unimolecular reaction was used to estimate the excess vibrational energy of cyclopropane.

In continuation of our photochemical project on cyclic molecules containing oxygen atom(s) in the ring,[2] we have studied the decomposition of tetrahydrofuran. In this molecule the carbon–oxygen bond strength is about 84 kcal/mol and it absorbs in the short ultraviolet. It is quite likely that the initial breakage of the carbon–oxygen bond upon absorption of light could lead to a diradical which, if excited, may decompose into "hot" end product(s). The purpose of this study is to examine the different modes of decomposition in this system.

Experimental

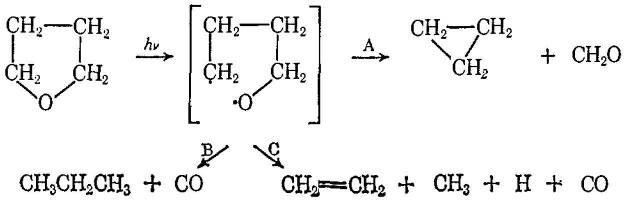
The apparatus used in this investigation has been described elsewhere.[2c] A Hanovia S-500 medium-pressure mercury arc was used as the light source. The tetrahydrofuran was an Eastman Kodak White Label grade compound. It was used without further treatment except for distillation under vacuum and drying over molecular sieves. For complete analysis of products, two runs were performed under each set of identical experimental conditions. In one run the product formaldehyde was quantitatively analyzed according to the procedure of Matsukawa.[3] The other run was used to analyze the rest of the products. For analysis of the products other than formaldehyde, the reaction mixture was condensed out of the reaction zone at −196°. The noncondensable products CO, H_2, and CH_4 were measured in a gas buret and analyzed quantitatively by a mass spectrometer. The composition of the condensable fraction was determined quantitatively by gas chromatography using a 25-ft silver nitrate–ethylene glycol (25% by weight on Chromosorb) column. These products were C_2H_4, C_2H_6, C_3H_6, c-C_3H_6, and C_3H_8. Small amounts of *n*-butane, butene-2, and butadiene were detected; no attempts were made to analyze these products quantitatively as their separations were inadequate. These products were never more than 4% of the total products.

Results and Discussion

The absorption spectrum of tetrahydrofuran vapor was analyzed semiquantitatively some time ago.[4] Two bands were noted in the region between 2000 and 1667 Å. The first band has a maximum at about 1900 Å (log ϵ 2.77), whereas the maximum of the second band lies at about 1739 Å (log ϵ 3.50). These bands are due to the excitation of 2p electrons of the oxygen atom in the ring. The photochemical decomposition of tetrahydrofuran was studied at the long-wavelength end of the first band. The medium-pressure mercury arc lamp exhibits four weak lines below 2200 Å (2003, 1973, 1942, and 1849). When a Vycor filter (5% transmission at 2200 Å) was used, no detectable amount of decomposition was observed. This, together with the fact that the onset of the first absorption band is about 2000 Å, indicated that photochemically effective wavelengths are below 2200 Å, and most important among these are at 1973 and 1942 Å, as all of the 1849-Å line will be absorbed by the long air path between the lamp and the reaction cell.

The runs reported here were carried out in the pressure range 10–165 mm with the variation of temperature from 30 to 120°. It was noted that the analyses of formaldehyde from the 30° runs were not reproducible as formaldehyde tends to polymerize at such a low temperature.[5] Therefore, most of the runs were done at 120°. The major products of decomposition were CO, H_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, c-C_3H_6, and CH_2O, together with minor products, C_4H_{10}, butene-2, and butadiene. In most of the experiments the amount of conversion was kept less than 1% to avoid secondary decomposition of the products. In the absence of a suitable actinometer below 2000 Å, the formation of CH_2O + CO was used as an internal actinometer in this system. Therefore, product yields were plotted as the ratio of the decomposition product, $X/CH_3O + CO$, *vs.* pressure.

The mode of decomposition of tetrahydrofuran may perhaps be best represented by eq 1. The carbon–oxygen bond strength in tetrahydrofuran is of the order of 84.1–85.2 kcal/mol[6] and, therefore, will be the first one to break. Since the excitation energy was about 145 kcal/mol, the energy carried over from the primary act was about 70 kcal/mol. Thus, the initially formed diradical was expected to be highly excited at least to the extent of 70 kcal/mol, and, consequently, could decompose to give a variety of products. However, decomposition of the initial diradical depends on the lifetime, which in turn will depend on the total pressure and



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[1] Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] (a) B. C. Roquitte, *J. Phys. Chem.*, 70, 2863 (1966); (b) *ibid.*, 70, 2699 (1966); (c) *J. Chem. Phys.*, 38, 4 (1963).

[3] D. Matsukawa, *J. Biochem.* (Tokyo), 30, 386 (1939).

[4] L. W. Pickett, *et al.*, *J. Am. Chem. Soc.*, 73, 4865 (1951).

[5] S. Toby and K. O. Kutschke, *Can. J. Chem.*, 37, 672 (1959).

[6] J. H. S. Green, *Quart. Rev.* (London), 15, 125 (1961).

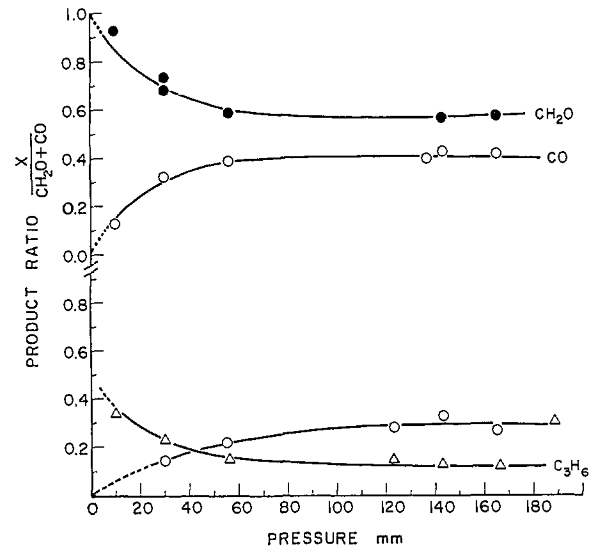


Figure 1. Effect of pressure on the distribution of products. X = CH_2O, CO, c-C_3H_6, and C_3H_6.

temperature of the system. Pressure-dependent behavior of the yields of CH_2O, CO, c-C_3H_6, and C_3H_6 are shown in Figure 1, and those of ethylene and hydrogen are shown in Figure 2. It is quite clear from Figure 2 that the yield of CH_2O was decreased to about 40% owing to an 18-fold increase of pressure. If CH_2O and c-C_3H_6 were formed by the same fragmentation step, then one would expect the yield of cyclopropane to decrease in the same fashion. However, this may not be the case if c-C_3H_6 is vibrationally excited, and stabilization by collision would occur with an increase of pressure; consequently, the yield of c-C_3H_6 would increase with pressure. Indeed, this was observed experimentally. It is interesting to note that the yield of C_3H_6 went down with pressure, and this should be the case if C_3H_6 was formed from vibrationally excited c-C_3H_6. Further discussion of the isomerization of vibrationally excited c-C_3H_6 to C_3H_6 and estimation of excess energy in this system are deferred until later.

The increase of CO yield with pressure was, at least in part, due to the preferential enhancement of the cleavage of the initial diradical by process B. Such a behavior may be expected if more than one vibrational level of the initial diradical were responsible for the three modes of decomposition. The decrease of the yield of C_2H_4 (Figure 2) with an increase of pressure was due to the removal of C_2H_4 by radical (CH_3, H) addition to the double bond, and also to the fact that process C tends to be less important as it is taking place from higher vibrational levels. Since process B, occurring from lower vibrational levels, becomes more important at higher pressure, one would expect the yield of C_3H_8 to increase also. Unfortunately, it was not possible to obtain quantitative data on C_3H_8 because of analytical difficulties.

The diradical concept in the tetrahydrofuran system can be supported by the observed similar modes of decomposition of 2,5-dihydrofuran.[7] The major products in this system were C_3H_6 and CO, and this clearly indicates the necessity of the postulation of a diradical intermediate which could decompose according to eq 2 to yield the observed products. Here the diradical A decomposed after rearrangement of the hydrogen atoms.

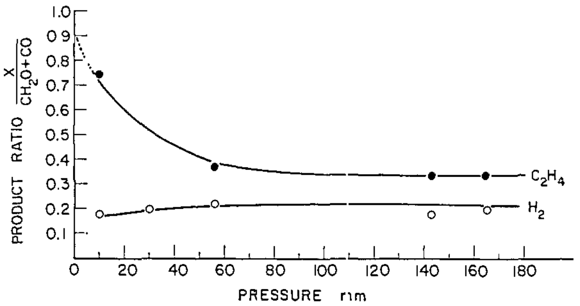


Figure 2. Effect of pressure on the distribution of products. X = C_2H_4 and H_2.

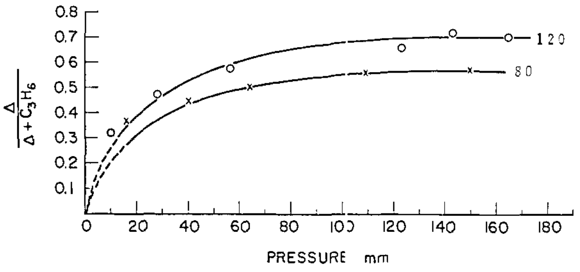
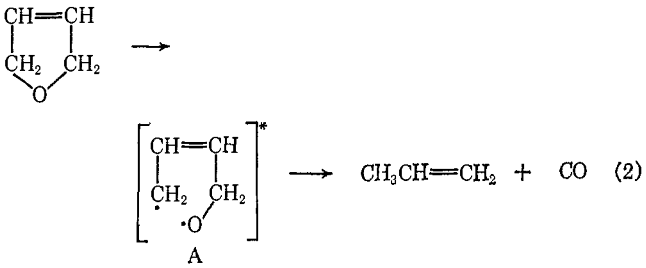


Figure 3. Effect of temperature and pressure on the fractional yield of cyclopropane.

The behavior of the hydrogen yield with pressure is not well understood at this time. However, it is certain that at least a portion of H_2 resulted from the secondary decomposition of CH_2O, as the yield of CH_2O was found to decrease with reaction time.



Excess Energy of Product Cyclopropane. The fractional yields of c-C_3H_6 at temperatures 80 and 120° and at different pressures are shown in Figure 3. The noteworthy features of such a plot are that the fractional yield of c-C_3H_6 increases with pressure and attains constant values at two temperatures. At 80 and 120° the limiting c-C_3H_6 yields were 0.58 and 0.70, respectively. Such a behavior of a product is indicative of the existence of a vibrationally excited product which could be deexcited with an increase of pressure by collisions. Since thermally[8] and chemically produced excited c-C_3H_6[9] was known to isomerize to C_3H_6, it was expected that an increase of yield of c-C_3H_6 will be met with a simultaneous decrease of the yield of C_3H_6. This is noted in Figure 1. If all of the C_3H_6 is assumed to have formed from c-C_3H_6, then the ratio $\Delta/(\Delta + C_3H_6)$ would have been unity at the high-pressure limit. On the

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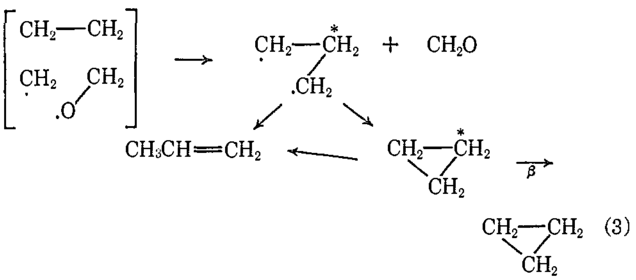
(7) E. J. Schmidt and B. C. Roquitte, submitted for publication.

(8) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (London), **A217**, 563 (1953).

(9) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957); H. M. Frey, *Proc. Roy. Soc.* (London), **A251**, 575 (1959).

other hand, if a fraction of C_3H_6 were formed directly from tetrahydrofuran, then this ratio would be less than unity at the pressure where c-C_3H_6 was collisionally stabilized. In fact, this ratio is less than unity at both 80 and 120°. Therefore, a fraction of C_3H_6 was produced by a pressure-independent process which, of course, was affected by temperature. It appears reasonable to suggest the mechanism in eq 3 to explain this particular observation. The existence of trimethylene diradical in the thermal isomerization of c-C_3H_6 has been suggested before.[10] If the trimethylene diradical was excited, then it would isomerize, at least in part, to C_3H_6 by a pressure-independent process. From the data given in Figure 3, it is inferred that the major fraction of this diradical was converted to excited c-C_3H_6, which was collisionally deenergized at high pressures.


(3)

An estimate of the excess energy of c-C_3H_6 may be made in the present system. This type of computation involves the use of the experimental rate constant which is given by

$$k_a = \frac{P_i - P_\infty}{\Delta_\infty}\beta$$

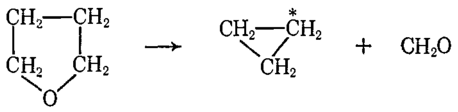
where P_i and P_∞ are the yields of C_3H_6 at initial pressure i and final pressure ∞, respectively, Δ_∞ is the yield of c-C_3H_6 at pressure ∞, and β is the collisional rate constant. Using the experimentally determined rate constant in the Kassel equation,[11] which is given as

$$k_a = A\left[\frac{E - E_{act}}{E}\right]^{s-1}$$

where A is the frequency factor, E is the total energy of the molecule, E_{act} is the activation energy, and s is the number of effective oscillators in the molecule. Substituting $A = 10^{15.17}$ sec^{-1}, $E_{act} = 65$ kcal/mol, $s = 13$, and $k_a = 6.01 \times 10^{-7}$ sec^{-1}, the total energy, E, of the cyclopropane molecule was found to be 86 kcal. The classical equation of Kassel has been used successfully in other systems. However, a more accurate equation for the estimation of excess energy was given by Rabinovitch, *et al.*,[12] following the concepts of the elegant theory of unimolecular reaction by Marcus–Rice. In his formulation of the equation for excess energy calculation, Rabinovitch has taken into account the zero-point energy of the energized and activated molecule and has assumed all vibrational modes to be equally active. This equation is given as

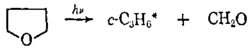
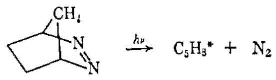
$$k_a = A\left[\frac{E - E_{act} + \alpha^{+}E_z^{+}}{E - \alpha E_z}\right]^{s-1}$$

where E and E_z^{+} are the zero-point energies of the energized (49.04 kcal/mol) and the activated complex (42.8 kcal/mol), respectively; α^{+} and α are empirical corrections; the other quantities have the same significance as in the Kassel equation. Using experimental values for k_a and the values for other quantities from the literature,[13] the estimated value of E was found to be 79 kcal, taking $E_{act} = 65$ kcal/mol and $s = 21$. It may be noted that the latter equation gave a value for E which is about 7 kcal/mol lower than that obtained from the Kassel equation. It was pointed out before[12,13] that lower values are usually obtained using the concept of zero-point energy and assuming all vibrational modes to be equally active. Since the over-all reaction is 28 kcal endothermic, and the excitation energy is 145 kcal/mol, the excess energy of 115 kcal/mol may be carried over to the products. As the estimated excess energy of cyclopropane was in the range 79–86 kcal/mol it is quite likely that the remaining 29–36 kcal/mol may excite the vibrational modes of other products in the system.



A comparison of the vibrational energy distribution in different systems is given in Table I. It is evident from these data that the major portion of excess energy goes to the product with the most vibrational degrees of freedom. For instance, in the present system, 75% of the estimated excess energy energizes cyclopropane. In the case of 2,3-diazabicyclo[2.2.1]hept-2-ene, 77% goes to C_5H_8 and the remaining 23% flows into other degrees of freedom.[14]

Table I. Comparison of Excess Energy in Primary Products

Reaction	Energy carried over from primary process, kcal	% of energy entering complex product	V_p/V_R[a]
	~115	75	64
	~100	77	85

[a] Ratio of the vibrational modes of product to reactant ×100.

At this point comparative analysis of the excess vibrational energy of cyclopropane products in other systems is called for. It is well known that photolysis of ketene and diazomethane in the presence of ethylene produces excited cyclopropane.[15] A recently estimated value of the energy of vibrationally excited cyclopropane is 103 kcal/mol in the ketene–ethylene system. This value is about 17–24 kcal/mol higher than that obtained in the tetrahydrofuran system. This is borne out quite

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(10) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, 38, 18 (1963).

(11) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932.

(12) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, 40, 1425 (1962).

(13) B. S. Rabinovitch and J. H. Current, *J. Chem. Phys.*, 35, 2250 (1961).

(14) T. F. Thomas, *et al.*, *J. Am. Chem. Soc.*, 89, 5107 (1967).

(15) H. M. Frey, "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, pp 217–233; see this article for other references.

conclusively by the experimental result that collisional deactivation was achieved at much lower pressure here than in the ketene–ethylene system.[9] Also, the average lifetime of the vibrationally excited cyclopropane was of the order of 10^{-7} sec, which is about three orders of magnitude lower than that obtained in the former system. However, the lower lifetime value is in accord with the value obtained in the thermal isomerization of cyclopropane[16] at 445°.

In summary, it should be pointed out that, although there is no direct evidence for the existence of a diradical in the tetrahydrofuran system, it was necessary to postulate such a species from the nature of the decomposition products. The initial diradical is formed with excess vibrational energy, and its decomposition path is dependent on the total pressure in the system. At least one product, cyclopropane, exhibited a behavior of "hot" molecule. However, its energy content appears to be significantly less than that obtained in the methylene–ethylene system, and the lifetime is similar to that in the thermal decomposition of cyclopropane. Further study of the photodecomposition of other members of the cyclic ether system are under way and may help in establishing conclusively the importance of a diradical mechanism.

(16) B. S. Rabinovitch, *et al.*, *J. Am. Chem. Soc.*, **81**, 1981 (1959).

Thermal Isomerization of 1-Methylcyclobutene at Low Pressures[1]

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Contribution from the Department of Chemistry, The University of Rochester, Rochester, New York.

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Abstract: The homogeneous, gas-phase, thermal isomerization of 1-methylcyclobutene to 2-methyl-1,3-butadiene has been studied in a 12-l. vessel at 150° for initial pressures from 1.1 to 0.004 mm and from 1.0 to 0.001 mm at 175°. In this pressure range the first-order rate constant decreases as the initial pressure is lowered: at 0.024 mm, the rate constant at 175° has decreased to about one-half the rate constant at 1 mm, and at 150° to approximately four-sevenths the value at 1 mm. At 175° the rate constant for 0.0015 mm has decreased to about one-sixth that at 1 mm. The decrease in rate constant for 1-methylcyclobutene at 175° occurs about $^{1}/_{20}$th to $^{1}/_{25}$th the pressure observed by Hauser for a comparable decrease of the cyclobutene rate constant at 150.4°. The curve showing the relative falloff of the rate constant with decreasing initial pressure of 1-methylcyclobutene at 175° lies close to the curve for the results of Frey and Marshall for 3-methylcyclobutene at 123.5°. The present results are compared with the predicted dependence of the rate constant for 1-methylcyclobutene on pressure, calculated by Elliott and Frey using RRKM theory.

The thermal isomerizations of cyclobutene and its alkyl derivatives into the corresponding 1,3-butadienes have been found to occur in the vapor phase at 130–200° as homogeneous unimolecular processes suitable for rate studies.[3–6] Moreover, the steric aspects of the isomerization and the kinetics of the liquid phase reactions of various cyclobutenes have been considered in a number of recent publications.[7]

The kinetics of the isomerization of cyclobutene in the gas phase have been investigated in the first-order region[3,8] and at lower pressures where the rate constant falls off.[3,9] The effect of methyl substitution upon the Arrhenius parameters of the reaction at moderate pressures has been studied by Frey and his coworkers.[4–6] A slight increase in the activation energy ($\sim$2.5 kcal/mole) and a lowering of the rate constant are produced by substitution of a methyl group in the 1 position,[4] and an effect in the opposite direction was observed for a 3-methyl group.[5] Over the pressure range of 5–150 mm the first-order rate constant for the isomerization of 1-methylcyclobutene into 2-methyl-1,3-butadiene underwent no change with pressure.[4] It was of interest to study the reaction at lower pressures and to compare the behavior of 1-methylcyclobutene with the results for related compounds. For 3-methylcyclobutene the decrease in the first-order rate constant with decreasing initial pressure has been determined in the region 45–0.01 mm.[10] Elliott and Frey[11] have calculated falloff curves for cyclobutene, 3-methylcyclobutene, and 1-methylcyclobutene by the use of the Marcus modification of the Rice–Ramsperger–Kassel theory and have compared the calculated curves with the existing experimental data for cyclobutene and 3-methylcyclobutene. Thus, the present study of the isomerization of 1-methylcyclobutene can provide a

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(1) (a) This work was supported by a grant from the National Science Foundation; (b) taken in part from the Ph.D. thesis of Margaret A. Karlsson, 1966.

(2) Holder of a National Science Foundation Summer Fellowship, 1960, and an E. H. Hooker Fund Fellowship, 1961–1962. Present address: ℅ D. A. Knecht, Division of Chemistry, National Research Council of Canada, Ottawa 7, Canada.

(3) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

(4) H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962).

(5) H. M. Frey, *ibid.*, **60**, 83 (1964).

(6) H. M. Frey, *ibid.*, **59**, 1619 (1963); G. R. Branton, H. M. Frey, and R. F. Skinner, *ibid.*, **62**, 1546 (1966); H. M. Frey, B. M. Pope, and R. F. Skinner, *ibid.*, **63**, 1166 (1967); H. M. Frey, D. C. Marshall, and R. F. Skinner, *ibid.*, **61**, 861 (1965); H. M. Frey and R. F. Skinner, *ibid.*, **61**, 1918 (1965).

(7) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965); R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **63**, 372 (1967).

(8) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **69**, 1073 (1965).

(9) W. P. Hauser and W. D. Walters, *ibid.*, **67**, 1328 (1963).

(10) H. M. Frey and D. C. Marshall, *Trans. Faraday Soc.*, **61**, 1715 (1965).

(11) C. S. Elliott and H. M. Frey, *ibid.*, **62**, 895 (1966).