ured here were independently checked by multiplying the solubility of AgCl (essentially equal to the concentration of $AgNO_3$ in a saturated equimolar solution) by γ_{AgNO_3} obtained by a short extrapolation of measurements of γ_{AgNO_3}[5-7] to the solute concentrations R'_{AgNO_3} and R'_{KCl} in a saturated equimolar solution. Values of log a_{AgNO_3} obtained thus are given in Table I and checked with the values plotted in Fig. 1 well within the errors in the measurements. For obtaining the slope, (d log $a_{AgNO_3}/d(1/T)$), the values plotted in Fig. 1 are probably more reliable. It might be noted that the fact that $a_{KCl} < a_{AgNO_3}$ in equimolar solutions of $AgNO_3$ and KCl is at least partly related to the conclusion that the species $AgCl_2^-$ is more stable than Ag_2Cl^+ in this solvent.[7]

TABLE I

SOLUBILITIES AND ACTIVITIES IN MOLTEN KNO_3 SATURATED WITH SOLID AgCl

T, °C.	$-\log s$	$-\log \gamma_{KCl}$	$-\log a_{KCl}$	$-\log a_{AgNO_3}$	$-\log (a_{AgNO_3} a_{KCl})$
350	2.787	0.274	3.061	2.997	6.058
370	2.652	.300	2.952	2.910	5.862
385	2.559	.322	2.881	2.839	5.720
402	2.456	.345	2.801	2.748	5.549
436	2.264	.409	2.673	2.590	5.263

Discussion

The heat of solution calculated from the experimental data using eq. 1 is $(10._{05} + 9._{15}) = 19.2$ kcal./mole with an estimated error of about 0.6 kcal./mole.

The heat of solution may be estimated theoretically from $(\Delta H_A + \Delta H_B + \Delta H_C)$. The heat change for the metathetical reaction A, ΔH_A, is calculated as 19.9 kcal./mole using the data in Table II and under the reasonable assumptions that the differences between the heat capacities of the reactants and the products and the variations of heats of fusion with temperature are small enough to be neglected. From the data of Kleppa,[12] the heat change for the dissolution process B is calculated as -303 cal./mole. Although the heat of solution of the hypothetical liquid KCl in KNO_3 is not available, an indication of the magnitude of the

(12) O. J. Kleppa, R. B. Clarke and L. S. Hersh, *J. Chem. Phys.*, **35**, 175 (1961).

heat of solution of such binary systems may be obtained from other thermodynamic measurements. The phase diagrams of the KNO_3–KCl[13] and the $NaNO_3$–$NaCl$[14] systems indicate an undetectable deviation from ideal solution behavior of the nitrate solvent at the liquidus temperature. This indicates that, for process C, the heat of solution, which usually parallels the excess free energies of solution, is probably small (less than 1 kcal./mole).

TABLE II

THERMODYNAMIC DATA FOR THE CALCULATION OF ΔH_A[a]

	Heat of formation of solid ΔH_{298}, (kcal./mole)	Heat of fusion ΔH_{Fusion} (kcal./mole)	Heat of transition ΔH_{TR} (kcal./mole)
$AgNO_3$	−29.43	2.76	0.66
AgCl	−30.36	3.16	—
KNO_3	−117.76	2.8	1.3
KCl	−104.175	6.1	—

[a] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," USNBS Circular 500, 1952.

Hence, within about 1 kcal./mole, $(\Delta H_A + \Delta H_B + \Delta H_C) = 19.6$ kcal./mole which, within the expected errors, is equal to the value of 19.2 kcal./mole obtained from the experimental measurements.

If the free energy values are available, the use of processes such as A, B, and C may be used to calculate theoretically the values of the activity product, a_{AgNO_3}-a_{KCl}, listed in Table I, since at saturation

$$RT \ln a_{AgNO_3} a_{KCl} = -\Delta F_A - (F^*_{AgNO_3} - F_{AgNO_3}°)$$
$$- (F^*_{KCl} - F_{KCl}°) = F^c_{AgCl} - F^*_{AgCl}$$

The Born cycle is not useful for estimating the activity product or the heats of solution because operational values of dielectric constants in molten salts are not available and even if measurable or meaningful must be known to a very high accuracy to lead to results as reliable and precise as are obtainable from consideration of processes such as A, B and C.

(13) E. Kordes, W. Bergmann and W. Vogel, *Z. Elektrochem.*, **55**, 600 (1951).

(14) E. R. Van Artsdalen, *J. Tenn. Acad. Sci.*, **29**, 122 (1954).

Recoil Tritium Reactions: Pressure-dependent Reactions with Cyclobutane[1]

BY EDWARD K. C. LEE AND F. S. ROWLAND

Recoil tritium atoms react with cyclobutane in the presence of O_2 scavenger to form mainly labeled cyclobutane, ethylene and HT. In the pressure range 0.07 to 1 atmosphere, the sum of cyclo-C_4H_7T and C_2H_3T yields is constant, but the fraction of this sum found as cyclo-C_4H_7T rises smoothly from 47% to 60%. In the liquid phase, the cyclo-C_4H_7T/C_2H_3T ratio is 4.6. The observed pressure dependence demonstrates the formation in the initial hot reaction of cyclo-C_4H_7T with sufficient excitation energy to cause unimolecular decomposition to C_2H_3T. The trend with pressure indicates a broad distribution of excitation energies for cyclo-C_4H_7T with a median energy of approximately 5 e.v. The initial specific radioactivity of the cyclo-C_4H_7T per H atom is approximately the same as that of CH_3T and n-C_4H_9T from the respective alkanes in direct competition in the same system.

Introduction

The chemical reactions of high kinetic energy tritium atoms have been investigated with a variety of hydrocarbons in order to establish the general characteristics of these hot reactions.[2,3] The study of reactions with

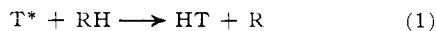(1) This research was supported by A.E.C. Contract No. AT-(11-)-407.

cyclopropane has been of special interest because of its known unimolecular isomerization to propylene, its

(2) M. Henchman, D. Urch and R. Wolfgang, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, Vol. 2, p. 83.
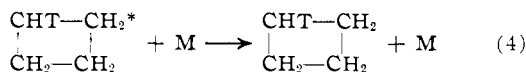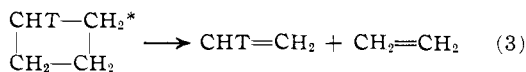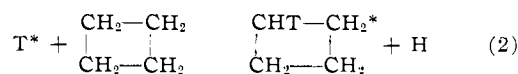
(3) F. S. Rowland, J. K. Lee, B. Musgrave and R. M. White, ref. 2, p. 67.

insensitivity to reactions with hydrogen atoms, and its cyclic character. The discovery of gas phase pressure-dependent yields of labeled cyclopropane and propylene has been interpreted as evidence for highly excited cyclopropane as a product of energetic tritium reactions, and provides qualitative information about the magnitude of the kinetic energy of the tritium at the time of reaction.[3-5] The interpretation of the reactions of recoil tritium with cyclopropane is made more complex by its insensitivity to attack by atoms and radicals, and by the possibility for the formation of radicals such as $CH_2T-CH_2-CH_2\cdot$ by direct energetic ring-opening reactions. When experiments with cyclopropane in the liquid phase showed a non-zero yield of radioactive propylene,[6] experiments were begun with cyclobutane in order to investigate further the variety of possible hot reactions with cyclane target molecules.
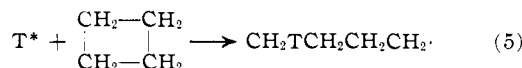
Among the pertinent reactions with cyclobutane are the energetic hydrogen atom abstraction 1

$$T^* + RH \longrightarrow HT + R \qquad (1)$$

the pressure-dependent reaction scheme 2 to 4

$$T^* + \begin{array}{c} CH_2-CH_2 \\ | \quad\quad | \\ CH_2-CH_2 \end{array} \longrightarrow \begin{array}{c} CHT-CH_2^* \\ | \quad\quad | \\ CH_2-CH_2 \end{array} + H \qquad (2)$$

$$\begin{array}{c} CHT-CH_2^* \\ | \quad\quad | \\ CH_2-CH_2 \end{array} \longrightarrow CHT=CH_2 + CH_2=CH_2 \qquad (3)$$

$$\begin{array}{c} CHT-CH_2^* \\ | \quad\quad | \\ CH_2-CH_2 \end{array} + M \longrightarrow \begin{array}{c} CHT-CH_2 \\ | \quad\quad | \\ CH_2-CH_2 \end{array} + M \qquad (4)$$

and the addition-with-ring opening reaction 5

$$T^* + \begin{array}{c} CH_2-CH_2 \\ | \quad\quad | \\ CH_2-CH_2 \end{array} \longrightarrow CH_2TCH_2CH_2CH_2\cdot \qquad (5)$$

In this case, unlike that of cyclopropane, the stable labeled products eventually resulting from reaction 5 are unlikely to be confused with those of reaction 3.

Experimental

These experiments have been carried out with cyclobutane as the target material in both the gas phase with He^3 as the tritium source under neutron irradiation, and in the liquid phase with Li^6 as the neutron target. The gas phase studies have been carried out over the range of cyclobutane pressure from 4.9 cm. to one atmosphere. Lower pressures are not feasible with the present experimental arrangement because of the necessity for having sufficient cyclobutane present to stop the recoiling tritium atoms in the gas phase. Both the convenient reactor facility and the available glass tubing limit the bulb size to 2 cm. i.d., while the necessary path length to stop the recoils is about 1 mm. cyclobutane at S.T.P. The upper pressure limit was also determined by the convenient reactor facility, whose operating temperature limited the pressure to values somewhat below the liquefaction pressure ($\sim$100 cm.).

As with the other hydrocarbon targets, the gas phase samples were prepared with about 1 cm. He^3, usually an added scavenger such as O_2, and finally the measured pressure of cyclobutane in bulbs of 12 to 15 ml. volume.[7] The liquid phase samples were condensed onto LiF contained in capillaries.[8] Both the gas bulbs and the capillaries were made from 1720 Pyrex glass because of its impermeability toward the back diffusion of tritium imbedded in its walls by the initial recoil.

The cyclobutane was purchased from Merck, Sharp and Dohme of Canada and showed approximately 4% n-C_4H_{10} and 0.3%

(4) J. K. Lee, B. Musgrave and F. S. Rowland, J. Am. Chem. Soc., **81**, 3803 (1959).

(5) J. K. Lee, B. Musgrave and F. S. Rowland, Can. J. Chem., **38**, 1756 (1960).

(6) E. K. C. Lee and F. S. Rowland, unpublished results.

(7) See J. K. Lee, B. Musgrave and F. S. Rowland, J. Am. Chem. Soc., **82**, 3545 (1960).

(8) E. K. C. Lee and F. S. Rowland, ibid., **84**, 3085 (1962).

C_3H_8 as impurities. Many of the experiments were carried out using this material directly; later runs (designated with numbers greater than 220 in the tables) were conducted with partially purified samples (n-C_4H_{10}, 0.2 to 1.2%). No difference was observed in the yields of major products for materials with varying impurity level, although the radioactivity level of the impurities themselves naturally was altered. The listed cyclobutane pressures in the tables are actually the sum of the pressures of cyclobutane and its impurities.

The separations and radioactivity analyses were carried out by the usual technique of gas chromatography and gas phase proportional counting, using helium and propane as flow gases.[9,10] Most of the measurements were made with an 85 ml. flow counter in order to increase the residence time, and therefore the number of counts observed, for each radioactivity peak. The more recent runs were made with a system incorporating a Digital Dynamics automatic printer for recording the data, replacing the Brush recorder used in earlier runs.

Two aliquots from each sample were separated and analyzed with different gas chromatographic columns: 80' acetonylacetone column at 0°, 50' Safrole column at 0°, 50' dimethyl sulfolane column at 24°, 50' propylene carbonate on alumina column at 0° and 8' silica gel at 80°.

In general, the agreement between analyses performed on different columns was excellent, and the identification of minor activity peaks is quite certain. Since the acetonylacetone column removes much of the acetylene from the gas stream it was not determined on all samples. Similarly, the propylene carbonate on alumina column also suffers a loss of radioactivity from $HC\equiv CT$ because of isotopic hydrogen exchange with the acidic substrate.

The neutron irradiations were carried out in the TRIGA reactor of the Omaha VA Hospital in a nominal neutron flux of 1.0×10^{11} n/cm.²/sec. The actual flux within Pyrex 1720 bulbs is considerably reduced by the high boron content of the glass, and the expected yield of tritium has been empirically evaluated from the total activity yields observed with several target molecules in which HT and readily-volatile hydrocarbons are the only tritiated molecules formed. Such evaluation indicates that the neutron flux in these bulbs for the gas phase runs was $5 \pm 1 \times 10^{10}$ n/cm.²/sec. This flux is in reasonable agreement with separate gold foil activation measurements of the neutron flux reduction within such irradiation bulbs. Calculations of expected activity from the liquid phase experiments are not very quantitative because of the heterogeneous irregular form of the capillary contents. Unless otherwise specified, all samples were irradiated for 1 hour.

Mass peaks were also recorded by thermal conductivity response for all runs. These values were useful in establishing the absence in scavenged samples of appreciable radiation alteration of the macroscopic contents. They also confirmed with an accuracy of about ±3% the measured ratios of components in the bulbs containing mixtures of hydrocarbons.

Results

Choice of a Standard for Expressing Relative Yields.
—The primary experimental effect sought in these experiments was the possible pressure dependence of cyclo-C_4H_7T and C_2H_3T, as from reactions 3 and 4. The first series of runs clearly showed a pressure-dependent yield ratio for these two products, and it immediately became desirable to have some pressure-independent internal standard against which the individual yields, as well as their sum, could be tested. Accordingly, three runs were made with O_2-scavenged mixtures of cyclobutane and methane, thus permitting direct comparison of each of the yields from cyclobutane with that of CH_3T from CH_4. The yield of the latter was expected to be pressure independent within the accuracy of previous measurements.[11]

The compositions of these mixtures and the actual radioactivity measured in each of the four chief products are shown in Table 1. The last row in the table shows that the sum of the radioactivity found as cyclo-C_4H_7T and C_2H_3T bears a constant ratio to that of CH_3T, when corrected for the relative amounts of the two parent molecules in the mixture. The increase in cyclo-C_4H_7T and corresponding decrease in C_2H_3T with rising pressure demonstrate the necessary relationships for the mechanism of reactions 1 to 3.

(9) R. Wolfgang and F. S. Rowland, Anal. Chem., **30**, 903 (1958).

(10) J. K. Lee, et al., ibid., **34**, 741 (1962).

(11) P. Estrup and R. Wolfgang, J. Am. Chem. Soc., **82**, 2661 (1960).

TABLE I

MAJOR RADIOACTIVE PRODUCTS FROM RECOIL TRITIUM REACTIONS WITH METHANE–CYCLOBUTANE MIXTURES

		No. 297	296	295
Gas pressures, cm.	Cyclo-C_4H_8	9.8	29.5	61.4
	CH_4	2.7	7.1	15.2
	O_2	0.5	0.7	1.1
	He^3	1.0	1.0	1.0

Observed radioactivity, counts[a]

Cyclo-C_4H_7T	12,620	19,330	18,700
CH_3T	3,040	3,710	3,540
CH_3T, corr.[c]	2,910	3,530	3,380
C_2H_3T	12,390	16,140	13,380
HT	43,700	58,040	52,150
R = (cyclo-C_4H_7T + C_2H_3T)/CH_3T	8.61	10.06	9.50
Specific activity ratio $RP_{CH_4}/P_{C_4H_8}$	2.37[b]	2.42	2.35

[a] Actual counts observed from 80' ACTN column with 44% of the sample. HT/CH_3T and C_2H_3T/C_2H_5T are divided on the basis of a 39% aliquot on 50' PCA. [b] The precision of mass ratios from measured mass peak measurement indicates an error of about ±3% in the pressure ratios used. [c] The yield of CH_3T from cyclo-C_4H_8 was 0.5% of the sum of cyclo-C_4H_7T and C_2H_3T. The observed CH_3T has been reduced by this ratio in calculating the yield of CH_3T from CH_4.

Two reasonably convenient methods for expressing recoil tritium data have been used in previous work[2,3]: (a) the observed yield relative to a convenient standard, often that of the parent molecule as 100, and (b) percentage of total tritium produced. Generally, inexact knowledge of experimental conditions, especially imprecision in neutron-flux information, makes the uncertainty in (b) much larger than the precision of relative measurements. Our data for O_2 scavenged systems are presented in terms of (a), choosing the *sum* of cyclo-C_4H_7T and C_2H_3T activities as our standard (=100). We have also listed the percentage of calculated total gas phase tritium activity found as cyclo-C_4H_7T to permit ready comparisons of scavenged and unscavenged systems.

Experiments with O_2 Present.—Previous experiments with hydrocarbons have adequately demonstrated that free radical scavengers, such as O_2, Br_2, I_2, etc., successfully eliminate thermal reaction contributions to labeled hydrocarbon yields with negligible effect on the energetic reactions proceeding concurrently in the same system.[2,3] Consequently, the primary data sought in these experiments have been in O_2-scavenged systems, as presented in Table II.

The cyclo-C_4H_7T and C_2H_3T yields are displayed in this table as the percentage cyclo-C_4H_7T contributing to the sum of both, with the error estimated solely from the statistical errors in the measurement of radioactivity. The yields and errors for HT are similarly calculated. The spread of the HT values in Tables II and III indicates some additional source of variation. However, the counting conditions were chosen to be favorable for the cyclo-C_4H_7T and C_2H_3T measurements, and were not optimum for HT measurement (high count rate, loss of resolution with long counter residence time).

Unscavenged Experiments.—Although the scavenged runs are most satisfactory for the purposes of these experiments because of the suppression of radiolytic damage as well as thermal reactions, many runs were performed in unscavenged systems and are summarized in Table III. The fraction of total tritium activity observed as cyclo-C_4H_7T was comparable at each pressure

for both scavenged and unscavenged runs, as shown in the final columns of Tables II and III. Assuming this yield as unaffected by scavenger, the data of Table III have been calculated relative to the yield of

TABLE II

RELATIVE YIELDS OF RADIOACTIVE PRODUCTS FROM RECOIL TRITIUM REACTIONS WITH CYCLOBUTANE IN O_2-SCAVENGED SYSTEMS

(Cyclo-C_4H_7T + C_2H_3T = 100)

Expt.	Gas pressure, cm. Cyclo-C_4H_8	O_2	He^3	Relative yields,[a] % Cyclo-C_4H_7T	HT	% total as cyclo-C_4H_7T
287	4.9	1.2	1.0	46.9 ± 0.9	150 ± 3	9
294	5.4	0.5	1.0	46.3 ± .7	154 ± 3	11
193	9.4	2.3	1.4	49.7 ± .7	151 ± 2	13
192	11.9	4.8	1.4	50.2 ± .7	147 ± 2	12
237	12.0	0.2	0.8	50.9 ± .8	169 ± 3	13
288	14.4	1.6	1.0	52.0 ± 1.0	149 ± 2	11
191	26.5	3.1	(1.4)[b]	53.5 ± 0.7	153 ± 2	(13)[b]
235	31.9	0.4	0.8	55.7 ± 1.3	164 ± 2	14
289	34.9	1.0	1.0	54.7 ± 0.7	157 ± 2	11
194	36.0	2.8	1.4	54.5 ± 0.7	154 ± 2	13
195	47	3.9	1.4	55.8 ± 1.2	158 ± 3	14
291	51.3	1.6	1.1	57.3 ± 0.7	151 ± 2	16
290	57.7	2.2	1.1	56.9 ± .7	150 ± 2	13
196	76.2	2.7	1.4	59.6 ± .7	153 ± 2	16

[a] All samples were irradiated for 1 hour at 5 × 10^10 n/cm.² sec. [b] He^3 measurement uncertain.

cyclo-C_4H_7T, with the latter assigned the value expected from scavenged runs. The C_2H_3T yields are then compared to the amount anticipated in scavenged systems at the same pressure.

TABLE III

RELATIVE YIELDS OF RADIOACTIVE PRODUCTS FROM RECOIL TRITIUM REACTIONS IN UNSCAVENGED CYCLOBUTANE

(i) Gas phase

Expt.	Gas pressures Cyclo-C_4H_8	He^3	Irradiation time, min.	C_2H_3T yield, % Expected	Obsd	HT, % yield	% total as cyclo-C_4H_7T
226	72.1	0.8	10	41.4	40 ± 2	251 ± 10	15
227	70.5	0.8	20	41.5	39.5 ± 1.6	257 ± 5	14
183	79.5	1.0	30	40.8	41.8 ± 1.2	237 ± 3	15
184	78.2	1.0	60	40.9	39.5 ± 1.1	247 ± 4	15
228	70.1	0.8	180	41.5	25.0 ± 0.7	234 ± 5	15
178	47.0	.9	30	43.6	42.6 ± 1.0	239 ± 3	15
180	52.8	.9	61	43.1	37.8 ± 0.8	229 ± 3	15
170	8.2	1.3	60	51.6	41.8 ± .7	216 ± 4	12
172	12.0	1.0	60	50.2	40.4 ± .6	207 ± 3	13
174	23.6	1.7	60	47.1	37.6 ± .5	230 ± 3	13
176	25.9	0.9	60	46.5	37.1 ± .7	232 ± 3	13
179	34.0	0.9	60	45.5	36.7 ± 1.0	240 ± 6	13

(ii) Liquid phase

Expt.			Cyclo-C_4H_7T	C_2H_3T	HT
200	Liquid with	60	83.0 ± 1.0	17.0	228 ± 5
201	LiF in	60	81.0 ± 1.0	19.0	239 ± 9
238	capillary	120	81.5 ± 0.7	18.5	211 ± 5

[a] Assuming cyclo-C_4H_7T/C_2H_3T ratio the same as for scavenged samples at the same pressure.

The one-atmosphere experiments with varying irradiation times demonstrate that radiolytic removal of

C_2H_3T becomes measurable within an hour, and is quite substantial for the three-hour run. However, the close agreement for C_4H_7T/C_2H_3T ratios and percentage yields in O_2-scavenged runs and the short-irradiation, unscavenged experiments clearly shows that the only appreciable effect of O_2 on the recoil reactions is in its expected role of scavenger for thermal species. All molecules in the system presumably serve with varying efficiencies as collision partners in reaction 4, and de-excitation in O_2 collisions has been included as given in footnote 17.

In lower pressure samples, the kinetic energy of recoil remains roughly constant while the amount of parent molecule is decreased. Although the total energy dissipated in the gas phase is lessened as the total stopping power in the gas bulb falls, the energy release in e.v. *per molecule* of parent increases steadily with decreasing pressure in these experiments, and radiolytic removal of C_2H_3T is observed for one-hour runs at all pressures.

The experiments with liquid phase cyclobutane are also included in Table III. Since radiolytic removal of unlabeled olefins is observed to be much less preferential in the liquid phase,[6] these results are normalized to the standard of cyclo-C_4H_7T + C_2H_3T = 100.

Discussion

Excited Cyclo-C_4H_7T Molecules as Reaction Products.—The data of Tables I and II show quite satisfactorily that there is a radioactive component that is found as cyclobutane at higher pressures and ethylene at low pressures in cyclobutane irradiations. The only
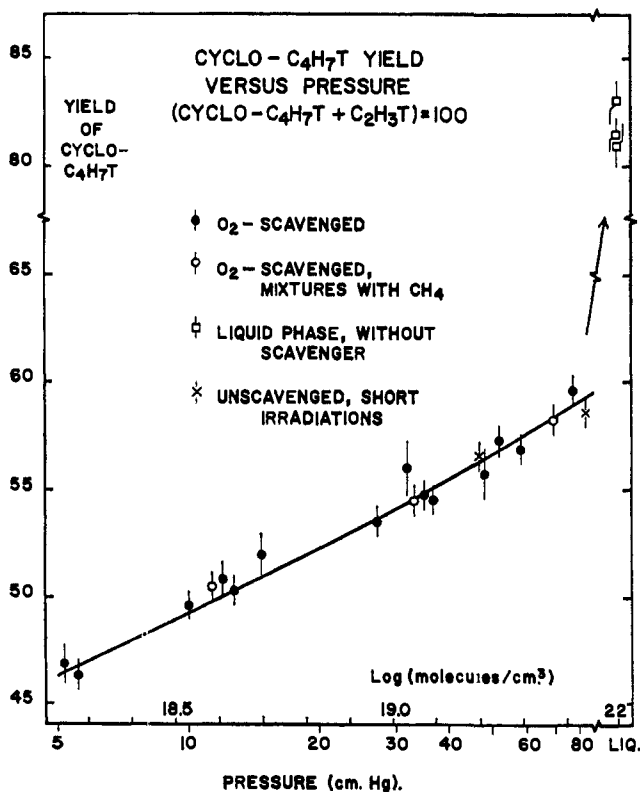
Figure 1.

isms of the true "hot" reactions,[3] the liquid phase differences can be expected simply as the consequence of an increase in the rate of reaction 4 from the much greater density of the liquid.

Since cyclobutane is a molecule that has been thoroughly studied in its pyrolytic decomposition, quantitative information is available about the rates of reactions 3 and 4.[12–14] Indeed, if the rates of decomposition and de-excitation are assumed equal for identical excitation energies in pyrolytic and recoil tritium systems, it becomes quite feasible to make some quantitative estimates of the energies involved in the recoil tritium system.[14,15] This assumption seems es-
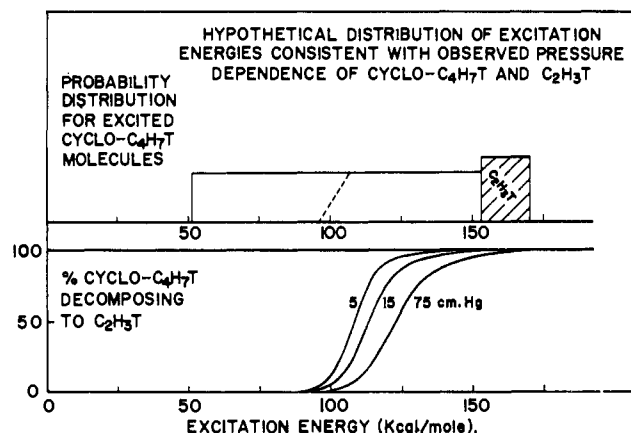
Figure 2.

pecially plausible in view of the close parallels already observed in similar cyclopropane systems between the pyrolytic isomerizations and those initiated by the highly energetic addition of methylene to olefins,[16] but has not yet been subjected to detailed testing.

The data of Tables II and III are presented in graphic form in Fig. 1.[17] This observed pressure dependence is much less drastic than that obtained in any of the systems involving the nearly monoenergetic molecules formed by photolytic addition of methylene to olefins. Consequently, the data of these recoil tritium experiments can only be consistent with the formation in reaction 2 of excited molecules of cyclo-C_4H_7T with a broad spectrum of excitation energies.

The solid line in Fig. 1 represents a calculated dependence of cyclo-C_4H_7T and C_2H_3T for the distribution of excitation energies shown in Fig. 2. Conversion of the distribution of Fig. 2 to a pressure dependence requires the choice of a suitable model for variation with energy of the unimolecular reaction rate, k_3: the classical Rice-Ramsperger-Kassel model was used here for convenience.[18] However, the model chosen serves only as a

(12) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951); F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S.*, **38**, 937 (1952); C. T. Genaux, F. Kern and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953).

(13) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (London), **218A**, 416 (1953).

(14) H. O. Pritchard and B. F. Gray, *J. Chem. Soc.*, 1002 (1956).

(15) Isotopic differences in reaction rates are expected between C_4H_8 and C_4H_7T. However, the magnitude of these differences is small relative to other errors in these estimates, and the observed parameters for C_4H_8 have been used directly with no isotopic corrections for C_4H_7T. See R. E. Weston, Jr., *J. Chem. Phys.*, **26**, 975 (1957), and ref. 14.

(16) See D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962), or J. Butler and G. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960), for two especially detailed comparisons.

(17) For plotting of total pressure, the partial pressures were added on the basis: cyclobutane, 1; helium, 0.1; methane, 0.5; oxygen, 0.2. The relative values for the first three were obtained from ref. 13, in which a value for O_2 was not measured.

reasonable mechanism that we can devise to account for this pressure dependence is that given in reactions 2 to 4, and we interpret the experimental results as confirmation of the correctness of this over-all reaction scheme. Since other comparisons of gaseous and liquid phase results have indicated a close similarity in the mechan-

connecting link between these experiments and the rates observed in pyrolytic and methylene–olefin systems. Since the latter processes are known to involve excitation energies in the range of 90–120 kcal./mole and rate constants sensitive to pressure near this range, every consistent model must lead to some broad spectrum of excitation energies centered around the 5 e.v. range, similar to that shown in Fig. 2.

The distribution of Fig. 2 really shows three separate groups of excited molecules. Broadly speaking, all molecules with excitation energies below 100 kcal./mole will be stablized as cyclo-C_4H_7T by collision before decomposition can occur—about 40% are shown in this group. The second segment constitutes those molecules whose decomposition rate is comparable to collision times in this pressure range. The fraction of molecules expected to decompose at each energy is given for three pressures in Fig. 2.[19] *All* of these molecules are assumed to be stabilized as cyclobutane in experiments carried out in the liquid phase.

The third segment, labeled C_2H_3T and shaded in Fig. 2, may not really represent decomposed cyclo-C_4H_7T molecules, since it represents the 18% of the sum of C_4H_7T and C_2H_3T that is always found as the latter in both gas and liquid phase experiments. Although decomposition of very excited parent molecules may well proceed in the liquid phase,[20] it is certainly possible that some other reaction mechanism is contributing all or part of the C_2H_3T yield.

The distribution shown in Fig. 2 is, of course, not the only distribution of excitation energies that will fit the data of Tables I and II. Almost any hypothetical division of the excited molecules with 40% below 100 kcal./mole, 18% for the C_2H_3T segment, and the remainder spread broadly over the 100–150 kcal./mole range would fit nearly as well. The proper deductions from Fig. 1 and 2 seem to us to be: (a) the substitution of tritium for hydrogen in energetic recoil tritium reactions is a process leaving substantial amounts of excitation energy on the labeled molecule formed in the reaction: and (b) in the particular case of cyclobutane, the median residual excitation energy is about 5 e.v., with a broad spectrum of actual energies.

Nature of the Reacting Entity.—In the absence of any direct evidence concerning the nature of the reactive tritium species, circumstantial evidence has been deduced to indicate that the recoiling tritium atom eventually reacts to form chemical bonds as a neutral ground state atom possessing excess kinetic energy.[2,3] Excitation energies in the range of 5 e.v. fit in well with this assumption of excess kinetic energy. They would not correspond, however, to the ≥ 10 e.v. or 13.6 e.v. expected if differences in the electronic or ionization state were involved between the entering tritium and exiting hydrogen atom of reaction 2. This evidence is again only circumstantial in the absence of any experimental measurements concerning the existence and pressure dependence of similar reactions initiated by $T(2s)$, T^+, etc.

Competition between Substitution in Cyclobutane and in Alkanes.—Recent experiments have demonstrated that energetic recoil tritium atoms substitute
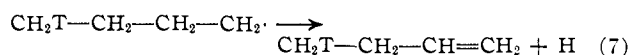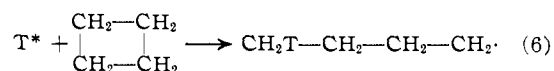
(18) These experimental values were used: $A = 10^{15.60}$ sec.$^{-1}$ (ref. 12), $E^* = 62.5$ kcal./mole (ref. 12), $\sigma = 5.5$ Å. (ref. 13). The parameter s was chosen as 19 from the close parallel in fall-off curves for methylcyclopropane and cyclobutane, as shown in J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960). De-excitation was assumed for reaction 4 on every collision, as in the original determination of the parameters.

(19) These percentages are calculated by the RRK model and are illustrative only of general trends. Calculations above about 120 kcal./mole are hypothetical by any model, since the photolytic methylene experiments cut off at about this energy; see ref. 16.

(20) By analogy with the excited hexyl radicals in E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 554 (1962).

approximately equally well for each hydrogen atom position in mixtures of CH_4 and n-C_4H_{10},[21] and thus show no evidence for any steric interference with such substitutions by adjacent alkyl groups.[2] The experiments reported here furnish an opportunity to compare substitution in cyclobutane with n-C_4H_{10} (present as an impurity), and with CH_4 as in Table I. Some uncertainty arises in performing such a comparison because of the uncertainty in the origin of all of the C_2H_3T. If 82% of the sum of cyclo-C_4H_7T and C_2H_3T yields is used as the "true" yield of cyclo-C_4H_7T, the specific activity ratios for cyclo-C_4H_7T vs. CH_3T and n-C_4H_9T are, respectively, 2.0 ± 0.1 (see Table I) and 0.79 ± 0.05 (runs 191–196 with 3–4% impurity). Both are in excellent agreement with the respective hydrogen atom ratios of 2.0 and 0.8. If all of the liquid phase C_2H_3T is included in the "true" cyclo-C_4H_7T yield, the ratios rise to 2.4 and 0.97. In either case, the specific radioactivity observed in cyclobutane is quite close, per H atom, to that measured for either CH_4 or n-C_4H_{10} in competition with it. Again, no evidence is seen for steric interference in the substitution process.

Formation of HT.—The relative amounts of HT formed in scavenged systems are reasonably constant, independent of pressure. However, as the percentage O_2 in the mixture is reduced, the HT yield rises, indicating that elimination of thermal or near-thermal tritium atom reactions cannot be accomplished with only traces of scavenger. In unscavenged systems, the thermal contributions increase the HT yield by about 50%.

Minor Products in Reactions with Cyclobutane.—The major labeled products from tritium reactions in a scavenged cyclobutane system are only HT, C_2H_3T and the cyclo-C_4H_7T. Small yields are found, however, of several other products, while many thermally-formed hydrocarbons have been identified in unscavenged reactions. The complete spectrum of products observed in several typical runs is given in Table IV.

TABLE IV

COMPLETE RADIOCHEMICAL ANALYSIS OF TYPICAL CYCLO-
BUTANE SAMPLES

Expt.	178	193	291	238
Cyclo-C_4H_7T	(56.3)	49.7 ± 0.7	57.3 ± 0.7	81.5 ± 1.0
C_2H_3T	42.6 ± 1.0	50.3 ± 0.7	42.7 ± 0.7	18.5 ± 1.0
HT	239 ± 3	151 ± 2	151 ± 2	211 ± 4
CH_3T	2.7 ± 0.3	0.6 ± 0.3	0.3 ± 0.2	5.2 ± 0.5
C_2H_5T	4.8 ± .3	0.2 ± .1	0.1 ± .1	9.7 ± .4
HC≡CT	0.9 ± .2	1.1 ± .2	(1.0 ± .2)^a	(0.5 ± .1)^a
$C_3H_7T^b$	5.2 ± .3	0.4 ± .1	0.5 ± .1	2.0 ± .2
C_3H_5T	0.8 ± .2	0.7 ± .2	0.7 ± .1	1.9 ± .2
n-$C_4H_9T^b$	8.3 ± .3	2.9 ± .2	0.9 ± .1	10.1 ± .3
C_4H_7T-1	2.5 ± .3^d	1.0 ± .2	1.8 ± .1	9.7 ± .3
i-C_4H_9T	0.6 ± .2	<0.1	<0.1	<0.1
1,3-C_4H_6T	0.9 ± .3	1.0 ± 0.2	0.9 ± 0.1	<0.5
i-$C_5H_{11}T$	1.4 ± .3	<0.2	<0.2	2.1 ± 0.2
A^c	<0.2			1.4 ± .3
B^c	$(5 \pm 1)^{a,d}$			2.3 ± .3

^{a} Measured for comparable samples. ^{b} Concentrations of C_3H_8 and n-C_4H_{10} impurities vary with the experiment. ^{c} Peaks A and B have not been positively identified. ^{d} The yield of these peaks decreases rapidly with irradiation time in unscavenged systems.

The yield of saturated hydrocarbons is essentially eliminated by O_2 scavenger, except for the yields arising directly from hot reactions with n-C_4H_{10} and C_3H_8 impurities. The observed yields of labeled butene-1 did not depend upon the impurity level of n-C_4H_{10}, and represent a bona fide hot product from cyclobutane,

(21) J. W. Root and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 3027 (1962).

presumably from reactions 6 and 7

$$T^* + \begin{matrix} CH_2-CH_2 \\ | \quad\quad | \\ CH_2-CH_2 \end{matrix} \longrightarrow CH_2T-CH_2-CH_2-CH_2\cdot \quad (6)$$

$$CH_2T-CH_2-CH_2-CH_2\cdot \longrightarrow \\ CH_2T-CH_2-CH=CH_2 + H \quad (7)$$

No conclusive statements are possible about the actual mechanism of reaction 7, which may involve an additional molecule, or may simply involve an energetic decomposition.

The butadiene, propylene and acetylene, however, come from especially energetic hot reactions and are not scavenger-sensitive.

The Infrared Spectra and the Nature of the Bonding in Some (1-Pyridine N-Oxide)-3-Ethylene-2,4-dichloroplatinum(II) Complexes
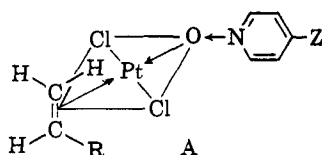
BY SAUL I. SHUPACK AND MILTON ORCHIN

The N^+-O^- and $C=C$ stretching frequencies of a series of 1-(4-substituted-pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) complexes, structure A, were determined. The N^+-O^- band in the spectrum of each N-oxide is shifted to lower frequency on complexing with platinum; the extent of the shift increases with increasing electron-releasing properties of the 4-substituent. The $C=C$ stretching frequency also shifts to lower frequency, and in an essentially linear fashion, with increasing electron-releasing properties of the 4-substituent, thus demonstrating the transmission of electronic effects across the platinum atom.
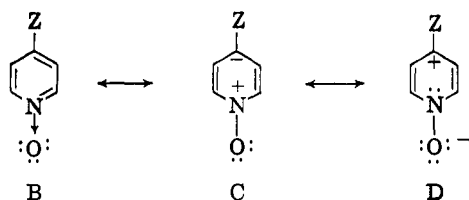
Introduction

Recent work in this Laboratory[1] showed that square planar complexes of platinum(II) of the general formula A can undergo exchange reactions in which the olefin or the N-oxide can be replaced by different olefins or N-oxides.

The infrared spectra of a series of these compounds (A, R = H; Z = NO₂, CO₂CH₃, Cl, H, CH₃ and OCH₃) has now been determined with a view toward securing information on the effect of ligand bonding as a function of the nature of Z.

Background.—Pyridine N-oxide can be represented by resonance forms C and D as well as by the principal structure B (Z = H)

The presence of electron-releasing groups (*e.g.*, Z = OCH₃) would be expected to enhance contributions from structures such as D. Such groups should therefore lengthen the $\overset{+}{N}-\overset{-}{O}$ bond and shift the infrared band associated with this bond to lower frequency as compared to the parent compound. Electron-withdrawing groups (*e.g.*, Z = NO₂) should have the opposite

effect. The reported infrared spectra of the pyridine N-oxides in chloroform,[2] in Nujol mulls,[3] and the spectra determined in the present work, Table I, confirm[4] this expectation.

TABLE I

DATA FOR 4-SUBSTITUTED-PYRIDINE N-OXIDE AND STRUCTURE A (R = H)

Substituent	pK_a	σ_p	$\overset{+}{N}-\overset{-}{O}$, cm.$^{-1}$ Ligand	Complex	$\Delta\gamma$, cm.$^{-1}$	$C=C$, cm.$^{-1}$
OCH₃	2.05[a]	−0.76[b]	1210	1190	20	1490
CH₃	1.29[c]	−0.31[b]	1238	1224	14	1500
H	0.79[c]	0	1242	1235	7	1510
Cl	0.36[d]	0.23[b]	1246	1238	8	1515
CO₂CH₃	−0.41[e]	0.64[f]	1252	1243	9	1528
NO₂	−1.7[c]	1.27[c]	1258	1250	8	1545

[a] J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1957). [b] Y. Okamato and H. C. Brown, *J. Am. Chem. Soc.*, **79**, 1913 (1957). [c] H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1955). [d] Calculated using σ-value from footnote *b* and ρ-value from H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958). [e] Calculated using σ-value from footnote *f*. [f] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

The effect of Z on the contributions from the various resonance structures also should be reflected in the basicity of the members of the series. Indeed, a linear relationship has been reported[5] to exist between the pK_a of a series of 4-substituted-pyridine N-oxides and the Hammett σ-value of Z.

(2) J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1958).

(3) G. Costa and P. Blasina, *Z. Phys. Chem.* (Frankfurt), **4**, 24 (1955).

(4) Our results, secured with mulls, corroborate the earlier work' except for the 4-nitropyridine N-oxide for which we obtained a doublet at 1258 and 1270 cm.⁻¹ as compared to the reported single band at 1271 cm.⁻¹. A doublet in this region has also been reported² for chloroform solutions of 4-nitropyridine N-oxide except that the bands were at 1283 and 1294 cm.⁻¹. For purposes of correlation of N^+-O^- stretching frequency we have chosen our 1258 cm.⁻¹ band because of its much greater intensity and because it appears from our correlations to be the band to be compared with other 4-substituted-pyridine N-oxides.

(5) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

(1) L. Garcia, S. I. Shupack and M. Orchin, *Inorg. Chem.*, **1**, 893 (1962).