equivalent to the photolysis of 2-hexanone in a D_2O "conditioned" cell. Since H_2O and hydroxylic compounds are more or less ubiquitous in comparison to –OD groups, the number of SiOH groups available for exchange in the experiments on 2-hexanone-d_2 probably greatly exceeded the number of SiOD groups available in the experiments on 2-hexanone. Hence reaction 3 may be expected to lead more often to the replacement of a deuterium by a hydrogen in the product in the photolysis of 2-hexanone-d_2 than the replacement of a hydrogen by a deuterium in the photolysis of 2-hexanone.

The term "intramolecular" as applied to the type II process may not be exact if the enolic form of the ketone produced frequently exchanges a hydrogen with some other molecule, in rearranging to the stable ketonic form. As a result, studies on the type II process with partially deuterated ketones are bound to give varied results according to (a) the nature of the walls of the cell and (b) the nature of trace impurities in the starting material. Since simple aliphatic ketones retain traces of water very tenaciously,[22] the presence of such contaminants may very well alter the nature of even a preconditioned cell, when the ketone vapor is introduced.[23] Conflicting results such as those on the photolysis of 2-pentanone-1,1,1,-3,3-d_5[7,8] may be explained in this way.

The increased yield of CH_3COCH_2D relative to CH_3COCH_3 in the photolysis of 2-hexanone-d_2 when an unfiltered mercury arc was used suggests that a reaction similar to (3) may occur in the gas phase at high intensities. This opens up interesting possibilities for further investigation.

Acknowledgments.—The author wishes to thank Professor W. Albert Noyes, Jr., for advice and encouragement during the course of this work, and Dr. William H. Saunders, Jr., for many stimulating discussions.

[22] K. S. Howard and F. P. Pike, *J. Chem. Phys.*, **63**, 311 (1959), discuss the difficulties in drying acetone.

[23] The contaminant may have –OH groups as in 2-hexanone-d_2 in the preparation of which no compound with an –OD group was used, or –OD groups as when D_2O is used to deuterate the α-carbon atoms of a ketone.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Thermal Unimolecular *cis–trans* Isomerization of *cis*-Butene-2[1]

BY B. S. RABINOVITCH AND K.-W. MICHEL[2]

RECEIVED MARCH 30, 1959

The unimolecular *cis–trans* isomerization of *cis*-butene-2 has been studied at 469° as a function of pressure, down to 3×10^{-3} mm. and up to 2000 mm. N_2. The fall-off region lies essentially below 2 mm butene-2. Activation energies were measured at four pressures between 5×10^{-3} and 100 mm. butene-2. $k_\infty = 6.1 \times 10^{13} e^{-62,800/RT}$ sec.$^{-1}$. Side reactions occur which strongly affect the observed kinetics above 10 mm. butene-2 pressure, but which are believed negligible below 5 mm. The observed unimolecular behavior is considered with respect to the Slater theory and is discussed in the light of other experimental findings on unimolecular reactions from the literature.

The first quantitative study of the *cis–trans* isomerization of *cis*-butene-2 by Kistiakowsky and Smith[3] gave the high pressure Arrhenius parameters $A = 2$ sec.$^{-1}$, $E = 18$ kcal./mole. Both internal evidence recognized by the authors, and external evidence, have suggested possible errors in this work. While the present study was in progress, Anderson, *et al.*,[4] reported a re-examination of this reaction and found $A = 10^{11}$ sec.$^{-1}$, $E = 52$ kcal./mole. The latter value approaches that for the singlet isomerization of ethylene-d_2 ($E = 65$ kcal./mole).[5] However the marked dependence of rate on pressure found by Anderson, *et al.*, just below one atmosphere led them to an anomalously low value for the lifetime of energized butene molecules.

The present study of this elementary reaction offers further clarification both of earlier work and of the status of this reaction as an illustration of a unimolecular process.

Experimental

Materials.—*cis*-Butene-2 was Phillips research grade. After purification it contained 0.026% *trans*-butene-2, 0.014% butene-1, 0.02% CO_2, 0.015% butane, 0.01% propane, 0.007% propylene. Propylene of the same grade contained only traces of CO_2 after treatment. Nitrogen, Linde's oil pumped grade, was passed through silica gel at −183° and then through a heated copper column.

Apparatus and Procedure.—A conventional vacuum apparatus was employed; a 175-cc. quartz bulb and a 4250-cc. Pyrex vessel served as reactors. Packed vessel runs were made in a 175-cc. Pyrex vessel, filled with glass wool. Reactors were heated in aluminum core furnaces. Temperature was read with chromel–alumel thermocouples calibrated against a standard. During a run, temperature was constant to 0.5° while the variation over the reactor was 0.5° in the small vessel and roughly 1° for the large reactor.

Rate studies were made as described. The reactor and lines were evacuated to 10^{-6} mm. or better. Hg vapor has no effect on reaction and was not excluded from the reactor. The desired pressure of butene (and addend if any) was admitted to the reactor. A sample for analysis was obtained after a given reaction time through a capillary sampling tube which first had been quickly swept out. At most pressures, five or six samples could be taken during one run with a pressure drop of not more than 10% (470°). At very low pressures, all material was frozen out of the reactor to provide sufficient sample. Runs were not carried beyond 15% *trans* isomer formation. The whole reactor was emptied at the end of a run for analysis of side products.

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[1] Abstracted in part from the M.S. thesis of K.-W. Michel, University of Washington, 1959. This work was supported by the National Science Foundation.

[2] Fulbright Exchange Fellow, Germany. Presently at Institute of Physical Chemistry, Goettingen.

[3] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 766 (1936).

[4] W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *ibid.*, **80**, 2384 (1958).

[5] J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

Analysis.—Most samples were analyzed by gas chromatography; *cis-trans* isomers were separated on a 3 m. column of 60% glycol saturated with $AgNO_3$ and a 40% dimethylsulfolane on firebrick. Side products were analyzed on a 4 m. column of dimethylsulfolane which separated them from the abundant main reaction products.

The lowest reaction pressure was determined by the minimum amount of gas which could be analyzed quantitatively, 0.006 cc. STP, setting a lower limit of 6×10^{-2} mm. in the small reactor and 3×10^{-3} mm. in the larger one (470°).

A Consolidated 21–103 mass spectrometer served for identification of polymer products.

Results

Handling of the Data.—The analytical and rate data were corrected for (a) dead space (usually less than 1%); (b) side reaction and small amounts of by-products; (c) small fluctuations in temperature. Rate constants were calculated from the equation for reversible first-order reactions. For the process *cis* $\rightleftharpoons$ *trans*, the equilibrium constant, K = 1.31, of Voge and May[6] for 700°K. was adopted. The constant does not vary appreciably over the temperature region employed. The lack of agreement on the magnitude of K is marked, but any error in the assumed value has negligible effect on calculated rate constants.

Standardization of the Reactors. Seasoning.—It was necessary to poison the reactors to obtain minimal and reproducible rates. Poisoning of the reactor walls at 469° with *cis*-butene-2 was complete after 30 min. at 20 mm. Overseasoning occurred if the reactor stood at 100 mm. for even 1 hr.; nitrogen had no deleterious effect. Long runs below 2 mm. pressure did not noticeably raise the rate of following ones, so that optimal seasoning was maintained. In practice, seasoning of the vessel so as to give reproducible rates was easily performed.

Autocatalysis.—Exploratory runs at pressures above 100 mm. revealed a monotonic acceleration of rate with time which increased with pressure. Typical results at 470° for total reaction times of 55 min. gave increases in k

At 100 mm. from initial value of	2.6 up to	2.7×10^{-5} sec.$^{-1}$
190	2.8	3.2
280	2.8	3.6
450	2.9	4.2

Below 5 mm. the rate constant was sensibly constant. Such autocatalysis, and its variation with pressure, is analogous to the behavior of ethylene-d_2[5] and presumably is a result of free radical catalysis of isomerization consequent on side reactions such as decomposition. The following observations make clearer the relation of these processes to the main reaction.

Side Reaction.—During a run at higher pressures the pressure decreased slightly and then increased by a few per cent. The principal side products were propene, butene-1 and a "C_7" unsaturate, together with very small amounts of ethylene, butane, "C_6" and traces of higher polymer.[7] The occurrence of propane[4] could not be confirmed. No analysis was made for methane or hydrogen.

The relative proportions of propene and butene-1 increased with time during a run, although the C_7 ratio was more or less invariant (Table I). Other characteristics which differentiate the polymer production were noted. The latter ratio decreased with increasing pressure, while propene and butene-1 production showed marked increase (Table I), of greater than first order.

TABLE I

EFFECT OF ADDENDS AND OTHER VARIABLES ON MAIN AND SIDE REACTIONS

P addend, mm.	P butene-2, mm.	T, °K.	% *trans*[a]	10^5 k,[b] sec.$^{-1}$	Ratio: side product/*trans* Butene-1	Propene	"C_7"
			Oxygen				
0	81	742.1	7.7	2.4	0.045	0.024	0.021
0.05	84		8.1	2.6	.051	.029	.023
0.33	89		9.1	3.0	.069	.040	.027
			Azomethane				
0	48	742.1	4.1	2.0	0.029	0.018	0.023
0.12	47		7.0	3.6	.074	.058	.034
0	4.5		3.5	1.69	.030	.017	.027
0.007	4.5		4.5	2.2	.049	.083	.078
0.10	4.5		6.3	3.2	.069	.130	.130
			Propene				
0	1.97	742.1	5.6	1.65	0.030	0.014	0.027
0.95	1.80		5.8	1.69	.023		.027
9.3	1.87		5.8	1.84	.020		.031
0	252		5.9[c]	2.6	.057	.025	.016
93	185		9.2[c]	2.8	.064		.017
			Packed vessel				
....	12	742.1	7.8	1.85	0.029	0.018	0.023
Packed	12		4.2	1.85	.015	.009	.021
....	93		10.2	2.4	.076	.033	.023
Packed	93		12.9	2.5	.031	.006	.015
			Time dependence				
	~265	742.1	3.09	2.4	0.044	0.025	0.017
			5.9	2.6	.057	.030	.015
			10.5	3.3	.077	.044	.015
			Temp. dependence				
	33.1	742.0	7.8		0.027	0.018	0.023
	14.0	706.9	0.73		.041		.030
	12.4	687.3	0.31		.054		.031
			Pressure dependence				
	0.15	742.1	5.4	1.37	~0.003	0.011	0.030
	.69		5.0	1.55	.028	.017	.032
	.73		5.4	1.63	~ .002	.011	.021
	4.5		5.7	1.76	.030	.017	.027
	43		8.6	1.96	.046	.023	.022
	93		10.2	2.7	.076	.033	.023
	445		12.4	3.8	.086	.040	.011
			Nitrogen				
104	33		16.9	1.83	0.029	0.028	0.030
425	51		6.8	2.1	.028	.019	.023
1043	51		6.8	2.2	.027	.018	.025

[a] Percentage of main product at end of run when side product was analyzed. [b] Refers to data of footnote *a*; differs a little from average value for the run or, at higher pressures, from the initial values. [c] The longer run time with propene (55 min.) compared with the blank (40 min.) must be kept in mind or the comparison of k, and the ratios, may be misleading.

The relative amount of side reaction to principal reaction increased with decrease of temperature, as would be expected if activation energies[8] for decomposition and polymerization of butene-2 are

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[6] H. H. Voge and N. C. May, THIS JOURNAL, **68**, 550 (1946).

[7] *Cf.* V. G. Moore, A. V. Frost and L. V. Shilyaeva, *J. Gen. Chem. USSR*, **7**, 818 (1937); D. S. Konovalov and E. N. Migotina, *Zhur. Priklad. Khim.*, **26**, 332 (1953).

[8] M. J. Molera and F. J. Stubbs, *J. Chem. Soc.*, 381 (1952); K. V. Ingold and F. J. Stubbs, *ibid.*, 1749 (1951). Rough activation energies for side reactions found here ranged around 57 kcal./mole.

lower than that for elementary isomerization found here. Earlier work[3,4] at lower average temperatures and higher pressures than those employed here would be more largely affected by side processes.

Special Tests.—A number of additional experiments were performed to assess the elementary nature of the isomerization and the importance of heterogeneity or catalysis under various conditions:

Packed Reactor.—Eleven-fold increase of surface/volume had no effect on the isomerization rate at 2 and 12 mm. (469°). At 93 mm. there was a possible slight increase. Packing reduced all three side reactions, particularly at higher pressure (Table I), which suggests chain inhibition. The behavior of "C_7" is contradictory. The decrease found with increasing pressure might indicate its origin in a wall reaction; the slight inhibition on packing the reactor refutes this assumption. The effect of packing also shows that although catalysis of isomerization must ultimately arise through side reactions, there is no linear correspondence between the amount of autocatalysis and of side product formation.

Oxygen.—Both the isomerization and, to a greater extent, the formation of butene-1 and propene are sensitive to oxygen (Table I). Air was carefully excluded, particularly since even traces led to deterioration of the seasoned surface.

Azomethane.—The influence of radicals was further investigated with azomethane (Table I). The effect of methyl in accelerating all processes is stronger here than in the isomerization of dideuterioethylene.[5] But analogously, the relative catalytic efficiency in the early reaction increases with decreasing pressure of addend; and the catalysis occurs strongly at the start time, corresponding to very rapid decomposition of azomethane. It also was found that the initial effect of radical addend is less at higher pressures of butene, for a given amount of azomethane (Fig. 1, curves a and c); but the sensitization does not stop with the initial formation and consumption of the radicals; the catalytic effect continues, stronger at higher butene-2 pressure. This indicates that formed radicals propagate their effect more efficiently at higher pressure. Side processes are more strongly accelerated by radicals than is the main reaction (Table I).

Propene.—Propene might also affect the reaction in contradictory ways analogous to the parent gas. On the one hand, it should inhibit radical catalysis; on the other, it could exert an accelerating effect due to self-decomposition. However this second effect should be less marked since the thermal stability of propene is greater than that of butene-2.[8]

The addition of small pressures of propene (0.9 and 9 mm. propene) to butene-2 at lower pressures (2 mm.) increased the specific rate of isomerization slightly while butene-1 formation was inhibited (Table I). In the higher pressure region (185 mm. Hg of butene-2 plus 93.5 mm. Hg of propene compared with 252 mm. butene-2) the effect was not pronounced.

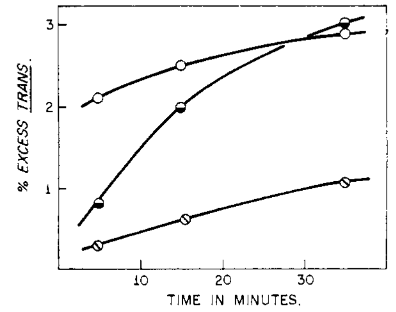

Fig. 1.—Per cent. excess *trans*-butene-2 above normal percentage in dependence upon time (468.9°): (a) 2.2% azomethane in 4.5 mm. butane-2, ○; (b) 0.16% azomethane in 4.5 mm. butene-2, ⦶; (c) 0.26% azomethane in 46.7 mm. butene-2, ◒.

Nitrogen.—Side product analyses were made in a few runs with inert gas. At the intermediate butene pressures noted in Table I, side reactions were somewhat inhibited by inert gas, analogous to the effect of packing.

Kinetic Data on Isomerization. Variation of Pressure.—The reaction was studied at 469° at pressures down to 3×10^{-3} mm. and up to 450 mm. butene (Table II). Judging from the pressure data alone the unimolecular high pressure region seems not yet to be realized. In anticipation of further inert gas data presented below, of the re-

TABLE II

PRESSURE DEPENDENCE OF ISOMERIZATION RATE CONSTANT

T = 468.9°

P, mm.	$k \times 10^5$, sec.$^{-1}$	Remarks
0.0030	0.60	Big bulb
.0031	.67	
.0047	.70	
.0051	.74	
.0052	.74	
.0052	.75	
.005	1.79	125.4 mm. N_2
.0074	0.78	
.011	.81	
.012	.86	
.040	1.01	
.066	1.05	
.154	1.37	
.173	1.26	Small bulb
.184	1.30	
.69	1.55	
.73	1.63	Big bulb
1.72	1.65	
1.85	1.72	
1.93	1.70	
2.0	1.73	Small bulb
3.2	1.80	124.6 mm. N_2
2.7	1.90	414 mm. N_2
2.5	1.99	2077 mm. N_2
4.5	1.76	
12	1.85	
48	1.96	
74	2.25	
81	2.4	
93	2.4–2.5	
280	2.6–3.3	
445	2.7–3.8	

jection of rate data at butene pressures above 5 mm. and of later discussion, it appears that the high pressure region is virtually realized at pressures of several mm. ($k_\infty = 1.90 \times 10^{-5}$ sec.$^{-1}$).

The Activation Energy.—Activation energies were determined at four pressures; at higher ones between 742.0 and 685.8°K., at the lowest one between 775.6 and 734.0°K. Arrhenius plots yielded straight lines with no evident curvature. The Arrhenius parameters were calculated by least squares. The data are summarized in Table III. The energy at 2 mm. is taken to be that of k_∞; it is at least a lower limit. Then $k_\infty = 6.1 \times 10^{13} \cdot e^{-62{,}800}/RT$. The decrease of activation energies above 2 mm. is opposite to the prediction of unimolecular reaction theory.[9] The apparent equality of activation energy at 5×10^{-3} mm. and at 1.76 mm. scarcely contravenes the theoretical decrease of E below E_∞ at lower pressures, in view of the small range of k/k_∞ encompassed by the experiments.

TABLE III

ARRHENIUS PARAMETERS FOR *cis-trans* ISOMERIZATION OF BUTENE-2

P, mm. (469°)	No. of (k,T) data	$E \pm \sigma$,[a] kcal./mole	$A \pm \sigma$,[a] sec.$^{-1}$
0.0047	11	62.4 ± 1.1	1.7 (±1.4) × 10^{13}
1.76	12	62.8 ± 0.9	5.6 (±3.3)
16.1	6	61.9 ± 1.2	3.0 (±2.5)
99	4	51.2 ± 1.9	3.0 (±3.9)

[a] Standard deviation.

Inert Gas Runs.—These data are of considerable importance. The addition of N_2 at low butene pressure restores the high pressure rate. The ratio of rates at 469° for pure butene-2 at 33 mm. and 5×10^{-3} mm. is greater than two-fold (Table II). However, one obtains the same rate (1.80×10^{-5} sec.$^{-1}$) at either pressure on adding 125 mm. N_2. By contrast, the average rate at 3 atm. N_2 + 1 mm. butene-2 was $k = 1.99 \times 10^{-5}$ sec.$^{-1}$ (rate constants constant with time), while for 450 mm. pure butene initial $k = 2.9 \times 10^{-5}$ sec.$^{-1}$ rising to 4.2×10^{-5} sec.$^{-1}$ in 1 hr. The relative efficiency of N_2, on a pressure basis, was roughly determined as 0.35 in two runs in which 0.9 mm. and 11 mm. N_2, respectively, were added to 5×10^{-3} mm. *cis*-butene. This number compares with relative efficiencies found for similar molecules.[10] The exact magnitude is unimportant; it is sufficient that 3 atm. N_2 may be considered conservatively as equivalent to 500 mm. of butene-2.

Finally, an increase of effective reaction pressure by a factor of 200 by addition of N_2 to 2.5 mm. butene-2 produces a concomitant increase in rate of only 14% (Table II).

Elementary Nature of Isomerization.—How much of the present isomerization data represents an elementary process? This section summarizes the evidence and arrives at a reasonably firm, although not indisputable, conclusion.

As direct evidence that isomerization is a simple elementary process at pressures below 2-5 mm. there may be cited: (a) The autocatalytic increase of rate during a run was absent below 5 mm. and bebecame most marked only at pressures above 100 mm. (b) The activation energy increases markedly from 51 to 62 kcal. on dropping the pressure from 99 to 16 mm., increases only slightly, if at all, from 62 to 63 kcal. on dropping from 16 to 1.8 mm. and is constant from 1.8 down to 5×10^{-3} mm. (c) At any butene-2 pressure below 5 mm., inert gas raises the rate to the same limiting value. This value is less than the rate for pure butene above 50 mm. (d) The plot of k *vs.* P is concave to the P axis below 8 mm. and approaches zero slope at pressures of 5–8 mm.; it has an inflection point in this vicinity.

Other evidence requires more detailed argument. The relative proportions of propene and butene-1 decreased as the pressure declined. Furthermore, since the amount of side products is not a *direct* measure of catalysis of the main reaction, the small amount of side processes at low pressures does not necessarily imply concomitant catalytic isomerization. This conclusion is plausible from the greater dependence on free radicals of side reaction relative to main reaction, demonstrated in the oxygen and azomethane studies. The same conclusion seems evident from the runs where the isomerization was unaffected by packing at 2 and 12 mm., although side reaction declined. Similarly, the addition of propene at 2 mm. butene-2 caused inhibition of the side reaction while accelerating the main reaction, presumably by inert gas effect.

Discussion

The Limiting High Pressure Rate.—The linear extrapolation of a Hinshelwood plot (k^{-1} *vs.* P^{-1}) does not give a good estimate of the limiting rate constant unless the data extend virtually to the high pressure limit. The plot has marked curvature and extrapolation gives an underestimate of k_∞. An improved extrapolation plot, k^{-1} *vs.* $P^{-1/2}$, has been proposed in the treatment of cyclopropane isomerization.[11] This plot, with curvature varying with the effective number of vibrational degrees of freedom, n, gives a more linear extrapolation. Figures 2 and 3 illustrate the superiority of this plot for extrapolation purposes over a Hinshelwood plot.

The linear representation of the data (Fig. 2) at 469° yields $k_\infty = 1.98 \times 10^{-5}$ sec.$^{-1}$. This value is beset with enough inaccuracy to allow for a small range of k_∞. Also, the straight line tends to be a slight overestimation of k_∞. Moreover, the possibility of slight acceleration by traces of oxygen in the inert gas run at the higher N_2 pressures cannot be excluded. For these reasons and those discussed in the next section, k_∞ is believed to be a little lower.

The Fall-off Parameter, *n*.—From the experimental fall-off, the Slater parameter n in the plot[12] of log I^n (θ) *vs.* log θ or log P may be determined.

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(9) (a) L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932; (b) N. B. Slater, *Phil. Trans. Roy. Soc.* (*London*), *N. Y.*, **246**, 57 (1953).

(10) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

(11) E. W. Schlag and B. S. Rabinovitch, to be published.

(12) The form of I_n (θ) and its dependence on θ is the same both in Slater's classical and quantum formulations (*Proc. Roy. Soc.* (*Edinburgh*), **54**, 161 (1955)).

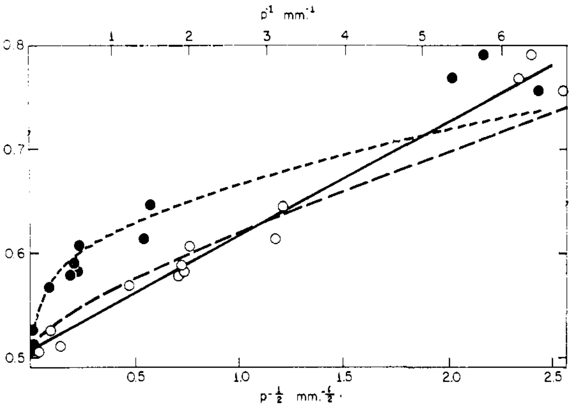

Fig. 2.—Comparison of plots of k^{-1} *vs.* $P^{-1/2}$, ○, and k^{-1} *vs.* P^{-1}, ●, close to high pressure limit. The dashed curves are theoretical for $n = 28$ and $\theta/P = 1.75 \cdot 10.^{17}$ The solid line is a least squares fit of the open circles.

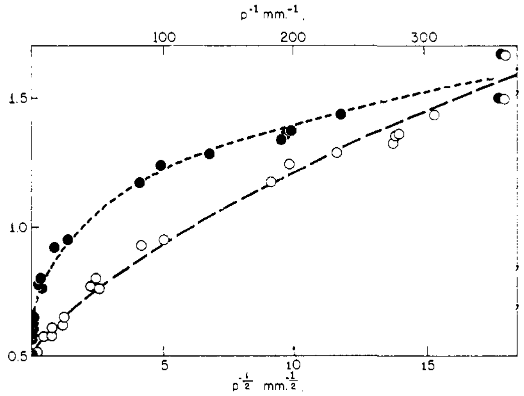

Fig. 3.—The comparison of the two plots as in Fig. 2 for the whole fall-off range studied.

The proper choice of k_∞ thus depends on points over the whole pressure range and not only on the very high pressure data. For this purpose, Slater's table[9b] of $I_n(\theta)$ has been extended[11] to $n = 30$. The experimental value of n may be quite sensitive to rather small variation in k_∞, as are other parameters of the reaction such as Johnston's F quantity, $<k_E>_\infty^T$, etc.[13] The value $k_\infty = 1.98 \times 10^{-5}$ sec.$^{-1}$ leads to $n \simeq 30$–31. Since $n = 30$ is the maximum value allowed, this sets an upper limit to k_∞. However, this value of k_∞ leads to unsatisfactory results for Johnston and White's consistency test,[13] $\nu_1\nu_3/\nu_2^2 > 1$, as well as an anomalously high value of $<k_E)_\infty^T$, relative to the same quantity for unimolecular reaction of simpler molecules. The value $k_\infty = 1.90 \times 10^{-5}$ sec.$^{-1}$ is well fitted by $n = 28$ (Fig. 4), yields a satisfactory result for the consistency test at all pressures and gives a value of $<k_E>_\infty^T$, based on conventional values of the collision constant, of 2.7×10^6 sec.$^{-1}$ which is more compatible with knowledge of other reactions.

The plot of k^{-1} *versus* $P^{1/2}$ is also useful in judging the optimum value of n for best fit, and the theoretical curves are shown in Figs. 2 and 3 for $n = 28$.

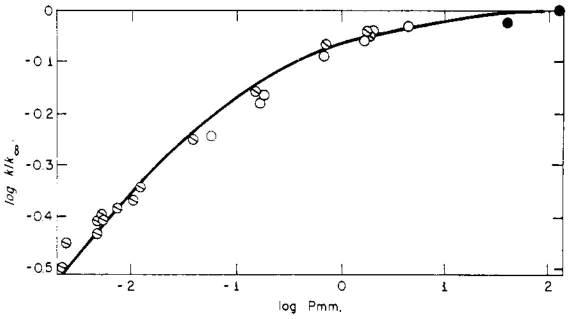

Fig. 4.—Fall-off plot, log k/k_∞ *vs.* log P_{mm}, at 468.9°. The experimental points are fitted for the Slater theoretical curve, $n = 28$: ●, N_2; ⦶, big reactor; ○, small reactor.

The data and above discussion illustrate two facts[14] which may still be insufficiently appreciated: (a) conventional or even excellent kinetic data frequently are inadequate to fix the shape of the fall-off exactly or to determine k_∞ precisely. For example as far as fit to a theoretical curve of log $I_n(\theta)$ *vs.* θ alone is concerned, then considering the inaccuracies of the data presented here, one could only say that n is determined approximately ($n = 28 \pm 3$ seems a reasonable estimate); (b) the molecular parameters that characterize a unimolecular reaction are very sensitive to errors in the experimental data.

θ/P and ν. — The parameter θ is related to pressure through the relation of Slater's classical case[9b]

$$\theta = (w/\nu)\mathrm{b}^{(n-1)/2} f_n$$

where the collision number w contains the pressure, and

$$f_n = \Gamma(\overline{n+1}/2) \times (4\pi)^{(n-1)/2} \times \prod_{i=1}^{n} \mu_i$$

$$\nu^2 = \Sigma\mu_i^2\nu_i^2, \ \Sigma\mu_i^2 = 1$$

and all other quantities are as originally defined. The experimental value of θ/P (mm.) for $n = 28$ is 1.75×10^{17}. The μ_i may in principle be obtained by an *a priori* calculation once the molecular reaction coördinate has been chosen. It appeared more discrete but yet of value to evaluate the magnitude and spread of the μ_i by a semi-empirical procedure.

cis-Butene-2 (symmetry point group C_{2v}) has no degenerate vibrations. The normal coördinate analysis of Kilpatrick and Pitzer[15] provides the necessary cognizance of the normal mode vibrations and frequencies. The weighting factors μ_i were assigned as follows: two internal methyl rotations were excluded. The μ_i were arranged in geometric progression such that $\mu_1/\mu_{28} = g > 1$. μ_1 was assigned to the normal vibration characterized roughly as double bond twist ($\omega = 402$ cm.$^{-1}$), and the next eight values were assigned to the remaining out-of-plane vibrations in order of proximity of frequency to that of the twisting motion (in effect from lower to higher frequencies). The in-plane vibrations were handled similarly. For $g = 6.0$, then $\theta/p = 1.73 \times 10^{17}$, $\nu = 4.2 \times 10^{13}$

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(13) H. S. Johnston and J. R. White, *J. Chem. Phys.*, **22**, 1969 (1954); the quantity $<k_E>_\infty^T$ corresponds to $<c>_{Av}^T$ in this reference.

(14) L. S. Kassel, *ibid.*, **21**, 1093 (1953).

(15) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **36**, 586 (1946).

sec.$^{-1}$. Since there are two reaction paths (giving rise to enantiomorphic transition states) $A = 2\nu = 8.4 \times 10^{13}$ sec.$^{-1}$. Variation of g by ± 1 causes departure of the calculated θ/P from the observed value by a factor ~ 3. The value 6 accords with Slater's earlier conclusion[9b] for simpler molecules (involving hydrogen in the molecular coordinate) that $g \sim 5$.

The above calculations are based on a classical treatment. It is of interest to see how treatment on a quantum harmonic oscillator model[12] changes the ν and θ/P values. The relationship among the relative magnitudes of the amplitude factors α_i is assumed the same as before. This model gives $\nu = 5.1 \times 10^{17}$ sec.$^{-1}$ and $\theta/P = 3.3 \times 10^{17}$. Exact agreement of θ/P with the experimental quantity results for a spread of α_i of 5.6 rather than 6.

Comparison with Other Unimolecular Reactions.—The value of n found for butene is close to the total number of vibration modes. A reasonable molecular reaction coördinate[9b] in the present instance is ostensibly a twisting skeletal motion. For ordinary ethylene itself, such a torsional motion corresponds to one of the three out-of-plane vibration modes[16] and n in this case of hypothetical "isomerization" would be (close to) unity. For substituted ethylene, *cis*-butene-2, the description of the corresponding normal mode as a twisting motion is approximate,[15] and a plausible *a priori* estimate of n might be nine, there being nine out-of-plane motions.

Similarly for isomerization of *trans*-ethylene-d_2, the experimental value of Kassel's s parameter was deduced (from rather scanty data) as 6 corresponding to $n \sim 10$, although $n = 3$ would appear to be a reasonable *a priori* estimate.[17]

It is useful to consider some other unimolecular reactions for which the data seem (with the limitations described above) established: e.g., the decomposition of cyclobutane,[13,18] the isomerization of cyclopropane to propylene,[19] the decomposition of N_2O_5,[13] of trioxymethylene,[10] and of nitryl chloride.[20] For all except the last reaction, a value of k_∞ has been obtained by extrapolation of a plot of k^{-1} *vs.* $P^{-1/2}$; the plot of log $I_n(\theta)$ *vs.* log P has been compared with calculated curves to obtain n.[21]

The values of n_{expt}, based on the shape of the fall-off at the high end of the range of k/k_∞, are collected in Table IV. In every case the Slater reaction and fall-off parameter n (of reference 9b) is a relatively large number $\leqslant t$, the number of molecular vibration modes. (It may be noted that the classical Slater and Kassel–Rice–Ramsperger integrals correspond[9b] formally at small n, if $n = 2s - 1$, where s is the Kassel parameter; however, numerical evaluation of both integrals by Mr. F. Schneider shows that as far as equivalent fit to observed fall-off, at the high end of the range of k/k_∞, is concerned, the value of s approaches and becomes $> n$ for larger n). Also, as indicated,[9b] in every case $n \leqslant t - d$, where d is the number of (doubly) degenerate vibrations, although it is quite doubtful whether the data are secure enough to make this observation firm. On the other hand, since in every case $n \sim t - d$, *a complex reaction coördinate seems always to be demanded.*[22]

The theoretical prediction of n for *cis*-butene-2 and for C–C rupture in cyclobutane would seem too small. It was seen in the former instance that unless some more complex reaction coördinate were taken, only 9, and not 28, modes might be expected to contribute. For cyclobutane, the Slater[23] theory analysis for the appropriate value of n (= 3) for the choice of C–C rupture as reaction coördinate in cyclopropane indicates that n would be predicted here also to be much less than the actual value.[24]

TABLE IV

EXPERIMENTAL VALUES OF EFFECTIVE NUMBER OF NORMAL VIBRATION MODES

Reacting molecule	Total vib. modes, t	No. of[a] degen. vib., d	$t - d$	n_{expt}[c]
NO_2Cl[20]	6	0	6	6
trans-$C_2H_2D_2$[b]	12	0	12	$\sim$10
cyclo-C_3H_6[19]	21	7	14	13
N_2O_5[13]	15	0	15	14–15
cyclo-C_4H_8[13,18]	30	7	23	20
cis-C_4H_8	30	0	30	28
Trioxymethylene[b]	30	10	20	$\sim$20

[a] The degenerate vibrations involved are in each case only doubly degenerate. [b] R. L. Burnett and R. P. Bell, *Trans. Faraday Soc.*, **34**, 420 (1938). [c] In an article which appeared since this paper was submitted, R. E. Powell, *J. Chem. Phys.*, **30**, 724 (1959), also has evaluated n for four of the examples which appear in the Table. For two of these, cyclo-C_4H_8 and trioxymethylene, our n values are appreciably higher than his. For a number of reasons we prefer our values It may be well to remark again, though, that the high values of n found for *cis*-butene-2 and other examples are not to be taken as precise. In addition to the experimental errors afflicting all n values, as discussed earlier in the text, Slater notes (reference 9b and private communication) the worsening of the approximations in his integral at higher n, particularly above $n = 15$.

If the evidence in Table III is indeed valid and general, this suggests the relevance of the fact that for larger amplitudes of motion the definition of normal vibrations tends to become more inexact. For large displacement in the reaction coördinate (torsion angle, θ, in the case of *cis*-butene-2), the effective configuration of a reacting molecule may be such that the ground state description of the normal vibrations loses pertinence. So, for ex-

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(16) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, New York, N. Y., 1945, p. 107.

(17) *Cf.* R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950), and the perturbation G sub-matrix for deuteroethylenes of lower symmetry than V_h.

(18) C. T. Genaux, F. Kern and W. D. Walters, THIS JOURNAL, **75**, 6196 (1953).

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

(20) H. F. Cordes and H. S. Johnston, THIS JOURNAL, **76**, 4263 (1954).

(21) The values used for k_∞ for cyclobutane and N_2O_5 differ from those given in reference 13 (for the conditions listed there) and are $k_\infty = 5.40 \times 10^{-4}$ sec.$^{-1}$ for cyclobutane and 0.50 sec.$^{-1}$ for N_2O_5. (These give rise to increased values of $\langle k_E \rangle_\infty^T$.)

(22) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959), discuss other evidence for the fact that most vibrations may enter into consideration in unimolecular reaction processes.

(23) N. B. Slater, *Proc. Roy. Soc.* (*London*), **A218**, 224 (1953).

(24) In a recent paper, E. Theile and D. J. Wilson, *Can. J. Chem.*, **37**, 1035 (1959), quote unpublished results by Srinivasan and Kellner which further confirm C–C stretch as the reaction coöordinate. In the present context, the large experimental value of n means a complex reaction coördinate of which C–C stretch is an important component,

ample, in the case of "isomerization" of ethylene mentioned above, the reaction coördinate for isomerization would appear to correspond closely to the normal torsional mode, as defined for the ground state. Now double bond twist in fact simultaneously involves change of C–C distance, etc. (see ref. 5); and although such interactions might be negligible for some purposes, as in the handling of small vibrations, the treatment of the reaction coördinate should take account of it, and in-plane as well as out-of-plane modes would be involved.

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[CONTRIBUTION NUMBER 183 FROM THE RESEARCH CENTER OF THE UNITED STATES RUBBER COMPANY]

Oxidation of Hevea Vulcanizates Containing Carbon Black[1]

BY E. M. BEVILACQUA

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The oxidation by molecular oxygen of a mixture of natural rubber and carbon black vulcanized with cumyl peroxide has been studied. Yields of volatile acid and of levulinaldehyde (at 140°) are independent of the presence or absence of carbon black. It is concluded: (1) the mechanism of rubber oxidation is not affected by the carbon, except as to rate; (2) volatile product yield gives an absolute measure of chain scissions which may be used to calibrate physical estimates; (3) an upper limit can be set to covalent bond formation during vulcanization involving reaction between allylic radicals and carbon, small compared to the total effective crosslink density. It is suggested that carbon black behaves as an antioxidant by virtue of reactions similar to those occurring with conventional antioxidants.

The oxidation of unvulcanized natural rubber and of other long chain polyisoprenes proceeds through cyclic peroxidic intermediates whose detailed structure depends upon the temperature of oxidation. The principal product is a hydroperoxide. At low temperatures high yields of stable hydroperoxides may be obtained. The structure of these was characterized by the work of Bolland and Hughes[2] on squalene peroxide. The structure of the "low temperature" peroxide formed in rubber has not been investigated directly because of analytical difficulties, but moderate yields can be obtained, and its properties are consistent with a structure similar to that formed from squalene.[3,4] At very high temperatures the predominant cyclic intermediate has a different structure from that formed at low temperatures.[5] It may not be converted to a stable hydroperoxide, but rather an intermediate radical decomposes directly,[6] leading to breakage of carbon-to-carbon bonds in the hydrocarbon chain. Associated with this decomposition is a group of low molecular weight compounds, including levulinaldehyde, formaldehyde and formic acid, acetic acid, carbon dioxide and (by inference) water.[5] The yield of each of the compounds depends to some extent on the experimental arrangement used to study their formation, but under a given set of conditions yields of one or more of these compounds form a good index of scission reactions in the hydrocarbon chain. So far as is known the ratio of scission to other reactions of the polymer with oxygen is determined solely by the temperature, through its effect on the ratio of "low temperature" to "high temperature" peroxide intermediates.

Using the correlation of index compounds with scissions as a means of studying the oxidation of vulcanized rubber,[7] it was found that no major change in the mechanism of breakdown of the polymer is introduced by crosslinking. The yields of volatile compounds per mole of oxygen reacted with vulcanized rubber are the same within experimental error as those obtained with raw rubber when allowance is made for the effects of temperature on product yield, in both peroxide-cured and efficient sulfur-cured vulcanizates. The vulcanizates used for the comparison were chosen to avoid complications arising from the use of inefficient vulcanizing systems. They gave the same relationship between solubility and swelling and between solubility and oxygen consumed as the conventional (Santocure[8] accelerated) gum compounds studied by Horikx,[9] implying the same scission mechanism for all vulcanized rubber.

A next logical step in the investigation of the detailed mechanism of the deterioration of rubber is the inclusion of the additional complication of fillers. This report describes a series of experiments with natural rubber containing carbon black (MPC), vulcanized with cumyl peroxide.

Experimental

Since results reported previously[7] have shown that the behavior of a peroxide vulcanizate and of an efficiently cured sulfur vulcanizate during oxidation are quite similar, for the work reported here the experimentally less complicated peroxide cure was used. Two different sets of samples were used in the course of this work. In the first set the

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[1] This is the sixth in a series on chain scission in the oxidation of Hevea. For the fifth, see ref. 7.

[2] J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

[3] E. H. Farmer and A. Sundralingham, *ibid.*, 125 (1943).

[4] B. C. Sekhar, *Rubber Chem. Tech.*, **31**, 425, 430 (1958).

[5] E. M. Bevilacqua, *Rubber Age* (*N. Y.*), **80**, 271 (1956).

[6] This conclusion is not fully established experimentally, but consideration of the structure of the probable intermediate[5] suggests that a "zipper effect" should be found, leading to high yields of low molecular weight products per apparent scission if the intermediate $RO_4\cdot$ resulting from successive additions of two oxygen molecules has significant stability. The observed yields instead correspond to a primary yield of one molecule of "scission products" per scission.

[7] E. M. Bevilacqua, THIS JOURNAL, **80**, 5364 (1958).

[8] Trademark name (Monsanto Chemical Company) for N-cyclohexyl-2-benzothiazole sulfenamide.

[9] M. M. Horikx, *J. Polymer Sci.*, **19**, 445 (1956).