peroxide. The infrared spectrum, taken neat, had absorption peaks at 3.40, 6.85, 7.20, 7.50, 8.90, and 10.5 μm. The peroxide gives a positive potassium iodide test and has a VPC retention time identical with that of a sample isolated from the electrolysis of 2-ethylhexanoic acid.

The peroxide was also obtained electrochemically. Sodium (1.5 g) was reacted with 150 ml of methanol, and 2-ethylhexanoic acid (52 g) was added. The solution was continuously saturated with oxygen and subjected to anodic oxidation at 1.0 A for 16 h. Water (100 ml) was added, and the resultant solution was extracted with four 125-ml portions of hexane. The hexane was dried over magnesium sulfate. After filtration the solvent was removed, and the residue was distilled yielding 6.0 g (7.2%) of the peroxide, bp 55–57 °C (0.15 mm). Analysis by VPC on a 6 ft × 0.25 in. SE30 on Chromosorb W column indicated the sample was contaminated with approximately 5% of 5,6-diethyldecane. Nevertheless, this sample was used in preparing analytical standards for determining peroxide yields.

The peroxide was shown to yield 3-heptanone and 3-heptanol on thermal decomposition as follows. A solution obtained from the electrolysis of 2-ethylhexanoic acid in the presence of oxygen was worked up in the described manner for the isolation of 5,6-diethyldecane. The high boiling residue was analyzed on an SE30 column at 140 °C and on a Carbowax column at 80 °C and shown to contain 5,6-diethyldecane, di-3-heptyl peroxide, 3-heptanone, and 3-heptanol. The product was sealed in a heavy walled glass tube and kept at 160 °C for 18 h. Analysis by VPC on the same two columns now showed the absence of di-3-heptyl peroxide, an unchanged amount of dimer, and a large increase in the amounts of 3-heptanone and 3-heptanol.

Thermal Stabilities of the Peroxides. The thermal stabilities were investigated qualitatively using VPC. By varying both the column temperatures and injection port temperatures, it was determined that both peroxides were reasonably stable at temperatures below 150 °C. At temperatures above 150 °C there was definite conversion of peroxide to aldehyde or ketone and alcohol. All VPC analyses were performed at temperatures below 150 °C. As a further safeguard the peroxide peaks for the standard solutions were matched as closely as possible to the peaks in the electrolysis solutions. In this manner, if decomposition does occur, the same amount occurs in both the known and unknown solution.

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Plasmolysis of 2-Butene

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Abstract: The reaction of *cis*- and *trans*-2-butene in a glow discharge was studied. The discharge was sustained with a 13.6-MHz radio frequency generator. The reactant at pressures from 0.01–10 Torr was flowed through the discharge region, and the products were collected and analyzed by gas chromatography. Under conditions which produce a low conversion rate (high pressure or low power), the exclusive products from *cis*-2-butene are *trans*-2-butene and 1-butene. Under conditions which give a high extent of reactant conversion (low pressure or high power), a different reaction channel producing propylene, acetylene, and ethane becomes favorable. It is suggested that the low conversion conditions produce electronically excited 2-butene by electron impact. Under lower pressure or higher power conditions more energetic electrons are available and produce more energetic intermediates. Plasmolysis of *trans*-2-butene gave *cis*-2-butene and 1-butene at low conversions and propylene, acetylene, and ethane under conditions producing high conversion. Experiments with added helium and argon (10 Torr) gave very similar results. It is shown, however, that isomerization is more favorable under these conditions. The negligible effects of added cyclohexane, naphthalene, and triethylamine demonstrate that $C_4H_8\cdot^+$ is not a trappable intermediate on the reaction pathway.

Recent studies, especially those by Suhr and co-workers,[2a] have demonstrated a number of unique and moderately high yield organic reactions which take place in a radio frequency discharge. This technique is interesting to us because it promises to provide a source of unusual intermediates, e.g., ions, in quantities sufficient for synthesis applications. There is, however, so little knowledge of the mechanism of reactions under these conditions that it is difficult to explore these possibilities in a rational fashion.

The basic mechanism for sustaining a discharge is established. It is known that a plasma, an ionized gas, exists in the discharge region, and it is accepted that organic molecules are primarily activated by electron impact.[2-5] Since conditions in the plasma are sufficiently energetic to ionize molecules, a wide variety of ions, radicals, and excited species are acceptable a priori intermediates. Indeed, the major mechanistic task is to design suitably discriminatory tests to determine which of these intermediates is actually along the reaction pathway.

The present investigation pertains primarily to the origin of products from 2-butene plasmolysis. Although the product mixture was at first disappointingly complex, it is a useful system to study because considerable complementary data

Table I. Plasmolysis Products from *cis*-2-Butene and *trans*-2-Butene

Run	Reactant isomer	Power, W	f,[a] mmol/min	Products, % yield[b] C_2H_2	C_2H_4	C_2H_6	C_3H_6[c]	Allene	1[d]	C_4H_{10}	*trans*-2	*cis*-2	Other[e]	Y_g[f]
1	cis	5	0.019	2.0	2.0	8.0	6.0	2.0	0.6	nd	0.7	15.0	2.0	0.4
2	cis	10	0.077	9.0	3.0	14.0	15.0	3.0	7.0	nd	3.0	43.0	4.0	1.0
3	cis	25	0.111	19.0	5.0	26.0	9.0	5.0	3.0	nd	1.0	16.0	5.0	0.9
4	cis	48	0.228	21.0	4.0	28.0	10.0	5.0	3.0	nd	1.0	23.0	5.0	1.0
5[g]	cis	25	0.229	N	N	N	3.0	N	12.0	2.0	10.0	59.0	3.0	0.9
6	cis	48	0.472	1.0	0.3	2.0	3.0	0.9	13.0	N	9.0	63.0	2.0	0.9
7	cis	25	0.153	11.0	4.0	18.0	9.0	2.0	8.0	nd	1.0	50.0	3.0	1.1
8	cis	25	0.378	N	N	N	0.4	N	3.0	N	3.0	93.0	N	1.0
9	cis	25	0.155	14.0	2.0	17.0	3.0	3.0	1.0	nd	0.6	20.0	2.0	0.7
10	cis	25	0.167	9.0	5.0	19.0	7.0	6.0	3.0	N	2.0	31.0	9.0	0.9
11[g]	cis	25	0.142	7.0	3.0	10.0	11.0	8.0	5.0	N	2.0	30.0	2.0	0.8
12	cis	25	0.06	21.0	7.0	24.0	17.0	14.0	2.0	N	N	11.0	2.0	1.0
13	trans	25	0.253	1.0	0.5	2.0	5.0	1.0	7.0	N	81.0	3.0	3.0	1.0
14	trans	50	~0.2	20.0	4.0	34.0	13.0	9.0	4.0	0.3	10.0	2.0	5.0	
15	trans	25		23.0	6.0	35.0	12.0	5.0	3.0	nd	13.1	1.4	1.0	

[a] Flowrate of 2-butene. [b] Yield based on moles of *cis*-**2** passed through reactor. N = not detectable, nd = detected, but not quantified. [c] $CH_3CH{=}CH_2$ plus CH_3CCH. Independent analysis showed the latter was present in negligible amounts. [d] Butadiene has the same retention time as 1. Independent analysis for runs 5, 10, 11 showed the latter present in negligible amounts. In run 12 it was 17% of the peak area. In run 13 it was 40% of the peak area. [e] Minor gaseous products yield estimated from GLC peak areas. Liquid products are also formed and account for the remainder of reactant. [f] Y_g = moles of condensable, gaseous products/moles of **2** passed. [g] Reactor packed with Pyrex glass wool.

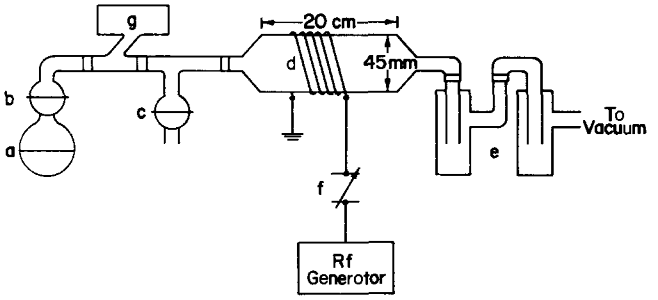


Figure 1. Plasma reactor: a, reactant; b, Teflon needle valve; c, inlet valve for added gas; d, 0.25-in. Cu tubing; e, liquid nitrogen traps; f, variable air capacitor; g, pressure gauge.

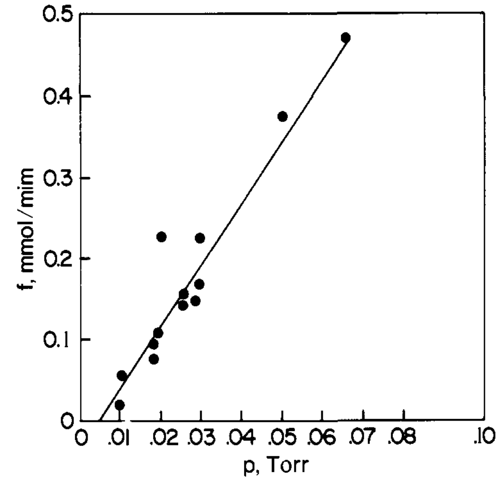
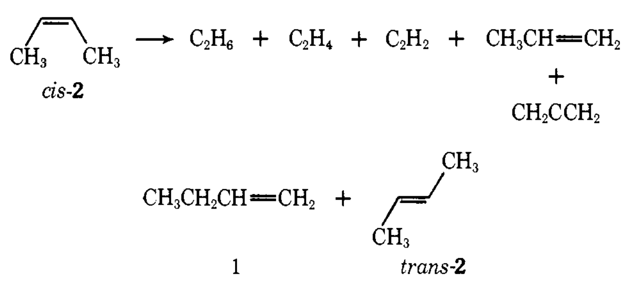


Figure 2. Correlation of flow rate and measured pressure for *cis*-**2**.

exists on the gas-phase reactivity of alkenes. We report here on reaction products and enucleate several mechanistic arguments. In particular cis-trans isomerization and trapping of intermediates are used as mechanistic probes, and plasmolysis products are compared in detail with those characteristic of certain reactive intermediates.

Results

The discharge apparatus described in the Experimental Section is schematically pictured in Figure 1. A bulb-to-bulb distillation at pressures from 0.01 to 10 Torr flows material through the discharge zone. A 13.6-MHz radio frequency generator supplies power to this region via a copper coil. After the material exits from the plasma region, it is collected in a liquid nitrogen trap and eventually analyzed by gas chromatography and/or spectroscopic techniques. In a typical experiment 250 mg of *cis*-2-butene (*cis*-**2**) passed through the apparatus in 30 min. The following equation qualitatively expresses the product mixture. No isobutylene was formed, and the yields of butadiene[6] and methyl acetylene were generally negligible. Yields were measured as a function of flow rate, *f*, and applied power and the data are collected in Tables I, II, and III.



Due to rf heating of the pressure transducer, it was not possible to make pressure measurements during a run. This difficulty was circumvented in part by measuring pressure before power was applied and correlating these measurements with the flow rate, *f*, during plasmolysis. As shown in Figure 2 a linear correlation exists (the correlation coefficient is 0.987 excluding one point). This proportionality suggests that although the pressure during plasmolysis is not accurately known, one can use flow rates to examine the pressure dependence. More importantly, the linearity of the plot indicates that Δt, the residence time in the reactor, is constant over this pressure range. Knowledge of the slope and the reactor volume (280 ml) allows one to calculate $\Delta t \simeq 80$ ms.

Figure 3 demonstrates that the extent of conversion of 2-butene depends on both the applied power and the flow rate (pressure). The fraction converted is defined as (1 − recovered 2-butene)/(initial 2-butene). Low power or high pressure gives low conversion.

Table II. Plasmolysis of *cis*-2-Butene at 25 W with Added Gas

Run, additive	P_{tot}, Torr[a]	$f \times 10^3$,[b] $\frac{\mathrm{mmol}}{\mathrm{min}}$	Y_g[c]	Products, % Yield[d]									
				C_2H_2	C_2H_4	C_2H_6	C_3H_6 + C_3H_4	Allene	1 + C_4H_6	*trans*-**2**	*cis*-**2**	C_4H_{10}	Other[e]
16, He	0.1	51.4	0.5	9.1	2.1	10.9	7.5	2.5	2.4	1.9	10.4	nd	2.4
17, He	4.0	184.0	0.9	N	N	N	0.7	0.6	8.0	15.2	67.3	N	1.2
18, He	4.0	57.0	0.5	7.5	3.1	8.0	6.0	2.4	2.8	3.9	14.0	0.5	1.4
19, He	10.0	120.0	0.3	5.9	1.2	6.0	3.5	2.0	2.1	2.8	8.5	0.5	1.2
20, Ar[f]	6.0	92.1	0.7	11.2	1.8	9.2	9.0	5.7	6.4	5.4	14.7	1.5	5.7
21, Ar[g]	6.0	44.3	0.6	6.3	1.1	6.2	6.3	2.6	5.3	7.2	23.0	1.4	3.1
22, Ar	10.0	163.0	1.0	0.4	N	0.6	1.0	0.6	2.1	3.4	92.0	N	N
23, Ar	12.0	70.0	1.0	N	N	N	N	N	0.2	0.3	99.6	N	N
24, Ar	6.0	nd	nd	20.2	5.2	0.9	3.4	4.4	1.7	1.1	58.9	1.7	2.5

[a] Total pressure measured before and after power turned on. [b] Flowrate of *cis*-**2**. [c] Y_g = weight of gaseous products/initial weight of *cis*-**2**. [d] Yield based on moles of *cis*-**2** passed through reactor. N = not detectable; nd = not quantified. [e] Other gaseous products. [f] Liquid product yield, 20% by weight; ratio of butadiene/1 = 0.2, ratio of acetylene/propylene = 0.1. [g] Liquid product yield, 23% by weight; ratio of butadiene/1 = 0.4, ratio of acetylene/propylene = 0.2.

Table III. Products from *cis*-2-Butene with Additives

Run, additive	P_{tot}, Torr[a]	Power, W	$f \times 10^3$,[b] $\frac{\mathrm{mmol}}{\mathrm{min}}$	Y_g[c]	Products, % yield[d]									
					C_2H_2	C_2H_4	C_2H_6	C_3H_6[e]	Allene	**1**[f]	*trans*-**2**	*cis*-**2**	C_4H_{10}	Other[g]
25, He, $C_{10}H_{10}$	5.00	25.0	46.4	0.4	2.5	0.6	4.2	6.7	1.7	3.8	2.5	11.5	0.1	1.5
26, O_2	0.09	25.0	94.5	1.0	15.3	5.3	20.3	14.3	5.0	4.5	3.9	33.7	N	1.8
27, acetone	0.06	25.0	112.0	1.4	2.4	2.7	55.4	12.0	2.5	0.9	0.5	60.7	N	N
28, Me_3N	0.30	70.0	228.0	1.0	N	N	7.8	7.4	7.4	1.8	1.4	79.4	N	N
29, H_2O	0.30	80.0	159.0	0.6	17.1	9.8	20.9	5.8	5.3	0.6	N	0.6	N	1.3
30, C_6H_{12}	0.04	55.0	46.0	0.6	30.7	9.7	20.2	2.6	1.5	0.4	0.2	0.3	0.3	0.5
31, C_6H_{12}	0.10	50.0	103.0	1.1	26.7	20.2	11.7	19.4	5.5	3.8	1.8	1.7	N	0.7
32, C_6H_{12}	0.04	25.0	176.0	nd	13.5	8.9	12.3	18.4	5.6	7.7	4.9	24.4	0.5	3.7

[a,b,c,d] Same as Table II. [e] C_3H_4 (methyl acetylene) was present in small amounts (<10%), the remainder was propylene. [f] Butadiene composed a negligible fraction of this GLC peak except in run 26 where it was 51%. [g] Other gases.

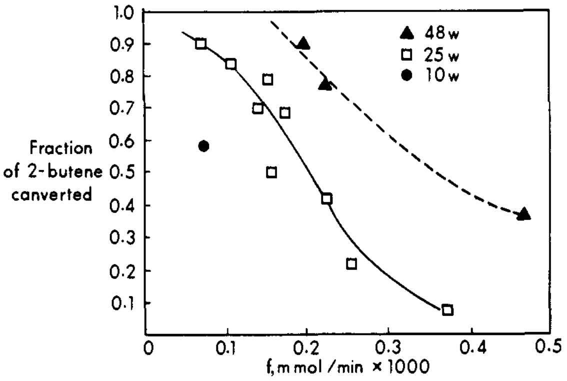


Figure 3. Reactivity of *cis*-**2** as a function of flow rate and power.

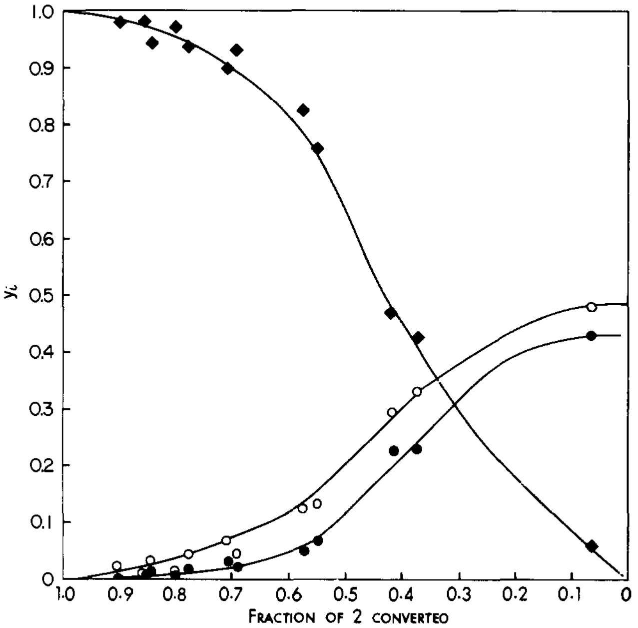


Figure 4. Products from *cis*-**2**: *trans*-**2** yield (●), **1** yield (○). Sum of C_2, C_3 product yields (■). Y = amount of product/total products not including *cis*-**2**.

The relative yields of products from *cis*-**2** vary widely depending on reaction conditions. These variations can be correlated with the extent of reaction as shown in Figure 4. In this figure Y_i = moles of product i/total moles of product excluding *cis*-**2**. When the conversion of *cis*-**2** is low, the products consist mainly of *trans*-**2** and 1-butene (**1**). At higher conversions, the products are primarily ethane, acetylene, and propylene.

The products from *trans*-**2** are virtually identical with those from *cis*-**2**, and again at low conversions isomerization predominates, fragmentation being more important at high conversions. Data from runs using *trans*-**2** as reactant fit the line established in Figure 4 for *cis*-**2**.

Experiments in which added helium or argon was used are compiled in Table II. The data, e.g., runs 16, 17, show that a similar trend to more fragmentation at high conversion exists in these experiments, as in those without added gas. Although the data are less complete, the added gas does appear to produce a higher relative yield of isomeric butenes at the same extent of conversion. A number of experiments with other additives were performed as well and these are collected in Table III. Addition of naphthalene (He carrier), trimethylamine, water, or cyclohexane did not have appreciable effects on either the conversion or relative product yields. These data points fall nearly on the appropriate line in Figure 3 or 4. The run with acetone showed decreased reactivity and a very high yield of ethane. This product, however, arises from acetone alone. The run with oxygen shows very similar products and conversions but larger amounts of butadiene. In the experiments with naphthalene and trimethylamine, most of the additive (>90%) was recovered unreacted, although there was a small amount of polymer formed in the naphthalene run and some unidentified nitrogen-containing liquid from the trimethylamine run.

The addition of a "carrier" gas alters the flow properties of the apparatus, as evidenced by the fact that, when the pressure of olefin is first established and inert gas then introduced, the flow rate of *cis*-**2** observed does not fit the line in Figure 2. Therefore, comparisons of the reactivity under these circumstances to that observed in the runs without carrier cannot safely be made. Another point of interest about the runs with argon or helium is that Y_g, the yield of gaseous products, is significantly lower than in the runs without carrier gas. That this is not due to loss of volatiles due to "carry out" by helium or argon is demonstrated by the good mass balance, and the fact that a known gas mixture from a previous run, when passed through the apparatus without rf power and at 15 Torr of helium, was recovered quantitatively with the ratios of components unchanged. In fact the drop in gaseous products (Y_g) was always correlated with a sharp rise in liquid products and, in the case of argon, polymeric products. Although it was established that these products were olefinic hydrocarbons, further characterization of their structures was not carried out.

To test for surface phenomena, the reactor was packed with Pyrex wool (Table I). The surface area was increased by approximately a factor of twenty in this way, yet there was no effect on the conversion or yield. These data points fall on the lines of Figures 3 and 4.

Discussion

Conversion Rates and Product Distributions. It is assumed in the following that in plasmolysis, molecules are activated by electron impact.[1-5] This produces intermediates which react and lose their energy by collisions. Because of the results using a packed reactor, we will ignore wall effects. Consider first the data on runs using *cis*-**2** as reactant with no carrier gas, performed at constant power, noting that the residence time is constant. Figure 3 shows that the conversion is strongly dependent on the pressure. At higher pressure less *cis*-**2** reacts. Two a priori explanations for this are (1) the rate constant for activation is lower at high pressure and (2) the activated *cis*-**2** molecules (I) are collisionally deactivated back to *cis*-**2** at high pressure. The latter possibility can be excluded because the change in conversion is much too large for the small variation in pressure. This follows from Scheme I. Where it is assumed

Scheme I

$$e^- + cis\text{-}\mathbf{2} \xrightarrow{k_1} \mathrm{I}$$

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_2} cis\text{-}\mathbf{2}$$

$$\mathrm{I} \xrightarrow{k_p} \text{products}$$

(1) that $[e^-]k_1$ and k_p are independent of pressure, (2) the concentration of quenching molecules (M) and activated molecules (I) is constant during a given run. The integrated rate expression corresponding to this scheme (where [*cis*-**2**] is millimoles of *cis*-**2** recovered) is:

$$\ln\left[\frac{[cis\text{-}\mathbf{2}]}{[cis\text{-}\mathbf{2}]_0}\right] = -k_1k_p/(\mathrm{m}k_2 + k_p)$$

In run 5 $-\ln([cis\text{-}\mathbf{2}]/[cis\text{-}\mathbf{2}]_0) = 0.53$, and in run 3 the same quantity is 1.83. Taking $M_6 = 2.07\ M_3$ (ratio of pressures or flow rates) allows one to write two equations and solve to find $k_p/M_3k_2 = -0.55$. This value demands a negative rate constant, illustrating that the argument does not fit the data. The pressure dependence must therefore result in part from a changing rate of activation.

In addition to analyzing the variation in conversion with pressure, it is also possible to treat the extreme variations in product composition in kinetic terms. Specifically the yields and conversions can be converted to relative rate constants using Scheme II.

Scheme II

$$e^- + cis\text{-}\mathbf{2} \xrightarrow{k_I} trans\text{-}\mathbf{2} + \mathbf{1}$$

$$e^- + cis\text{-}\mathbf{2} \xrightarrow{k_f} C_2H_2 + C_2H_6 + C_3H_6$$

$$e^- + trans\text{-}\mathbf{2} \xrightarrow{k_f} C_2H_2 + C_2H_6 + C_3H_6$$

In this scheme it is assumed that (1) the isomers *cis*-**2**, *trans*-**2**, and **1** do not significantly equilibrate, (2) that the rate constants for formation of *trans*-**2** and **1** involve one type of process so their rate constants can be summed as k_I, (3) the rate constants for formation of the various fragment products can be summed and treated as k_f, and (4) the rate constants for disappearance of *cis*-**2** and *trans*-**2** are equal. Assumption 1 is supported by the observation that there is never more than 10% *trans*-**2** formed from *cis*-**2** and never more than 10% *cis*-**2** from *trans*-**2**. Therefore, although interconversion is undoubtedly occurring, it is not an important kinetic factor. Assumptions 2 and 3 result from Figure 4 where the ratio of *trans*-**2** and **1** is seen to be relatively constant. Although there is considerable scatter in the ratios of fragmentation products, there is no apparent trend. They all increase at low pressure and are, therefore, summed for ease of treatment. Assumption 4 is supported by the conversions noted in runs 8 and 13.

Defining N_e as the number density of electrons, the scheme and assumptions give:

$$\frac{[cis\text{-}\mathbf{2}]}{[cis\text{-}\mathbf{2}]_0} = \exp[-(k_I + k_f)N_e\Delta t]$$

and the yield of butene isomers (Y_B = *trans*-**2** + **1**/all products) is:

$$Y_B\left(\frac{[cis\text{-}\mathbf{2}]_0}{[cis\text{-}\mathbf{2}]}\right) - 1 = \exp(N_ek_I\Delta t) - 1$$

Using these expressions the relative rate constants k_f/k_I can be calculated (Table IV). It is seen that there is considerable variation, k_f/k_I being large at low pressure. The origin of this variation seems to lie primarily in k_f as can be seen from the relatively constant values for $N_ek_I\Delta t$, but variable values for $N_ek_f\Delta t$ (Δt is constant throughout). A reasonable explanation for the dependence of conversion and products on pressure involves electron kinetic energies. At low pressures more high energy electrons are present. This produces either different or more energetic intermediates which fragment rather than isomerize. Since higher power levels will also shift the electron energy distribution, the general correlation between conversion and product distribution (Figure 4) can be rationalized. Our understanding of organic plasma dynamics is so lean that this rationale must be regarded with some skepticism. The observation that reactivity is strongly dependent on pressure is, however, extremely important. It demonstrates that casual surveys of reactivity may be quite misleading.

Although the same products, a similar conversion-product distribution relationship, and a similar *trans*-**2**/**1** ratio is seen when a high pressure (10 Torr) of helium or argon is used, there are subtle differences. It is important to note that the residence time and true partial pressure of *cis*-**2** are not accurately known in the experiments with a carrier gas. There-

Table IV. Effective Rate Constants ($N_ek\Delta t$) in the Plasmolysis of *cis*-2-Butene[a]

Run	Y_B	$\frac{[cis\text{-}2]_0}{[cis\text{-}2]} - 1$	$N_ek_I\text{-}\Delta t$	$N_e(k_I + k_f)\Delta t$	$N_ek_f\Delta t$	k_f/k_I
2	0.18	1.02	0.17	0.70	0.53	3.1
6	0.05	5.38	0.23	1.85	1.62	7.0
7	0.06	3.38	0.19	1.48	1.29	6.8
9	0.54	0.71	0.32	0.54	0.22	0.69
10	0.06	2.21	0.19	1.17	0.98	5.2
11	0.10	2.36	0.30	1.21	0.91	3.0
12	0.02	8.20	0.12	2.22	2.10	17.5

[a] Data from Table I, all at 25 W.

Table V. Effective Rate Constants for *cis*-**2** with Added Gas[a]

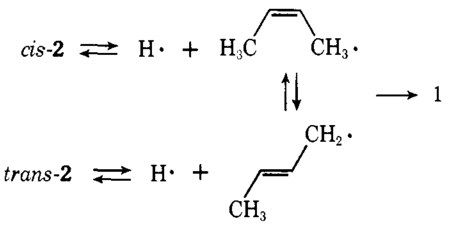
Run	Additive	Y_B	$\frac{[cis\text{-}2]_0}{[cis\text{-}2]} - 1$	$N_ek_I\Delta t$	$N_e(k_I + k_f)\Delta t$	$N_ek_f\Delta t$	k_f/k_I
13	He	0.047	8.61	0.34	2.26	1.92	5.6
14	He	0.713	0.48	0.29	0.39	0.10	0.3
15	He	0.078	6.14	0.39	1.97	1.57	4.0
16	He	0.053	10.80	0.45	2.47	2.02	4.5
17	Ar	0.138	5.82	0.59	1.92	1.33	2.2
18	Ar	0.160	3.34	0.43	1.47	1.04	2.4
19	Ar	0.677	0.09	0.06	0.09	0.03	0.5

[a] Runs at 25 W.

fore, quantitative comparisons will not be undertaken. Using Scheme II the relative rates of isomerization and fragmentation can, however, be calculated as before. Again it is found that at low pressure the rate of fragmentation increases while the rate of isomerization is relatively constant (Table V).

Comparison of Tables IV and V demonstrates that an equal extent of conversion and more isomerization results in runs with added gas. The difference may be attributed to differences in the electron energies or to energy transfer processes. Thus the "inert" carrier could, for example, be involved in Penning ionization, electronic energy transfer and collisional stabilization of excited intermediates. Indeed, considering the availability of argon metastables[7] for sensitization, the products are remarkably similar to those without added gas. A major difference is the increased yield of high molecular weight products.

Intermediates. Although a variety of species are undoubtedly present, we can only treat those involved in the final product-forming reactions. The above evidence suggests that one type of process leads to the two isomerization products and another to fragmentation. The specificity of the former demands that the carbon skeleton remain intact. Therefore, either an intra- or intermolecular 1,3-hydrogen rearrangement is required to form 1-butene. One intermolecular isomerization process is:



The virtual absence of disproportionation products butadiene, butane, and dimers makes this process improbable. The small effect of O_2 and organic additives on the reaction reinforces this conclusion. For the intramolecular reaction initially consider three[8] intermediates (a) $C_4H_8\cdot^+$, (b) $C_4H_8^*$ (electronically excited), and (c) $C_4H_8^{\ddagger}$ (vibrationally excited). The reactivities of these types of species have been previously characterized.

Ausloos and co-workers,[9] as well as others,[10] have produced $CH_3CHCHCH_3\cdot^+$ by a variety of techniques and studied its chemistry. Although fragmentation products are detected, no evidence for isomerization to $CH_3CH_2CHCH_2\cdot^+$ is obtained. Indeed, this 1-butene ion will instead isomerize to the 2-butene ion if it is sufficiently energetic. This is quite reasonable since the 2-butene ion is expected to be more stable. Thus, the evidence suggests that 1-butene cannot be accounted for by ionic isomerization. It could, however, be formed after an exothermic neutralization of the ion.

Turning now to a comparison with photochemical processes, there is considerable data on pertinent gas-phase photochemistry.[11,12] The product mixtures obtained from direct photolysis of *cis*-**2** at 200 nm and 20 Torr are quite similar to those obtained by plasmolysis. In particular 1-butene and *trans*-**2** are major products with propylene, acetylene, and ethane as significant minor products.[11] At higher total pressures using methane as an inert gas isomerization to *trans*-**2** and **1** is more dominant. Indeed, if a *linear* extrapolation to 0.05 Torr was assumed, it would predict that very little isomerization should be seen. It does seem important, however, that the contrathermodynamic isomerization of *cis*-**2** to **1** can be achieved photochemically at a rate as fast as that for formation of *trans*-**2**. This 200-nm process probably involves singlets. The triplet sensitized photolysis of *cis*-**2** has also been studied; and although there are similar fragmentation products, the major pathway is cis-trans isomerization.[12]

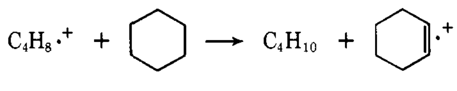
It should be noted that the plasma products from *cis*- and *trans*-stilbene are also suggestive of excited molecule reactions.[13,14] In particular the cis-rich mixture seems most consistent with electronically excited neutral precursors. In this case isomerization is much faster than other reactions and a near steady state mixture of isomers is achieved even at very low power levels.

The possibility of invoking vibrationally excited molecules can be examined using thermolysis data. The products from *cis*-**2** have been determined over a range of temperatures up to 1200 K.[15] At lower temperatures cis-trans isomerization is by far the dominant reaction pathway and even at high temperatures it is a major route. This does not correlate with the plasma results. Furthermore, the most important other product in thermolysis is butadiene which is a minor constituent from plasmolysis.[16] Since it is expected that the polychromatic electrons present in the plasma would produce a number of vibrationally excited states and that this energy would be rapidly distributed to other modes, thermolysis seems a sufficient model for vibrationally excited molecules, and the results are not consistent with this mechanism.

A further test which will discriminate for or against an ionic mechanism like (a) involves trapping. Thus Ausloos and co-workers have shown that $C_4H_8\cdot^+$ can be trapped by charge transfer from easily ionized molecules like triethylamine present in small amounts ($p < 0.01$ Torr):[9]

$$C_4H_8\cdot^+ + (C_2H_5)_3N \rightarrow C_4H_8 + (C_2H_5)_3N\cdot^+$$

In this reaction, the butene product can be isolated. The evidence strongly suggests that the $C_4H_8\cdot^+$ retain their structure upon quenching. A second very important quenching reaction is H_2^- transfer from alkanes to $C_4H_8\cdot^+$:[9]



This reaction is quite characteristic of alkene cation radicals. Its regiospecificity allowed strong support to be given to the concept that the $C_4H_8\cdot^+$ isomers are not rapidly equilibrating. Thus, for example, $CD_3CDCDCD_3\cdot^+$ formed $CD_3CHDCHDCD_3$ with cyclohexane.

These tests were applied to the *cis*-**2** plasma reaction (Table III). The presence of easily ionized triethylamine or naphthalene had no effect on the reaction. Neither did an excess of cyclohexane produce butane. A small amount is usually detected, but even this decreases slightly in the presence of cyclohexane. In all three cases, the bulk of the additive was isolated unchanged. This data rules out $C_4H_8\cdot^+$ as the sole intermediate (via pathway a, Scheme I). Scheme III is still allowed, but only if neutralization of $C_4H_8\cdot^+$ with electrons is faster than trapping.

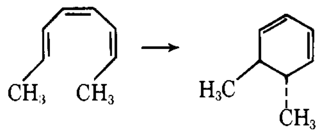
Scheme III

$$cis\text{-}\mathbf{2} \rightarrow {}_4H_8\cdot^+$$

$$C_4H_8\cdot^+ \rightarrow C_4H_8{}^*$$

$$C_4H_8{}^* \rightarrow \text{products}$$

A recent report by Kim and Thornton[17] is of particular interest in comparison to our results. They studied the stereochemistry of two electrocyclic reactions induced by an AC discharge between platinum electrodes. They found, for example, that *cis,cis,trans*-octatriene cyclized stereospecifically



to *trans*-cyclohexadiene in 5% yield. This stereochemistry is also found for pyrolysis but is not found for the corresponding photoisomerization. It was, therefore, concluded that electronically excited molecules were not involved and that hot ground states were likely precursors of the cyclohexadiene product. The similarity of experimental conditions and substrates and the dissimilarity of conclusions reached in that work and in this is both striking and inexplicable. It seems important to conduct more direct and detailed mechanistic tests in order to elucidate a mechanistic paradigm for plasmolysis. The difficulties in the photolysis–plasmolysis comparison used by Thornton and ourselves should be realized.[18]

The above arguments deal primarily with the isomerization pathway. Fragmentation is much more difficult to treat. Although these products are seen in the 200-nm photolysis, they also arise under other conditions. The nature of these products suggests radical intermediates. We propose to undertake plasmolysis of isotopically labeled compounds in the future to further elucidate the mechanism.

Experimental Section

Materials. *cis*- and *trans*-2-butene (Matheson, C.P.) were checked by gas chromatography prior to use. None of the other isomeric butenes could be detected by the flame ionization instrument, and purity was accessed at >99%. All other chemicals were obtained from commercial sources and similarly checked for purity prior to use.

Instrumentation. NMR spectra were taken on a 60-MHz Varian T-60 instrument, and ir data were obtained with a Beckman Acculab-3 infrared spectrometer. Some gas chromatography was carried out with a Varian Aerograph Model 90-P (thermal conductivity detector), but the bulk of the hydrocarbon analyses were done with a Bendix Model 2110 equipped with a flame ionization detector. The rf generator used to produce the plasma was an International Plasma Corporation Model PM105B, operating at 13.6 MHz, with power output variable from 0–300 W. The instrument is equipped with a watt meter and a Torr meter using a vacuum transducer.

Apparatus. The apparatus shown schematically in Figure 1 consists of a calibrated all-Pyrex vacuum system capable of being evacuated to a pressure of 10^{-4} Torr and an all-Pyrex reactor portion. The reactor portion is composed of several parts for ease in cleaning and weighing and is assembled by means of standard taper 14-20 joints with Apiezon N stopcock grease. The reaction chamber consists of a 45-mm i.d. Pyrex cylinder, 20 cm in length. This may be coupled to the rf generator in several different ways, but in the work reported here an inductive coupling was used (shown). A five-turn coil from ¼ o.d. in. copper tubing is connected via a balancing circuit (which consists of a variable capacitor or a capacitor–transformer combination) to the output of the RF generator.

With this configuration, there is a considerable problem with stray rf heating of the vacuum transducer during the course of the plasma runs, particularly at higher powers. Consequently, when this means of pressure measurement was employed, the pressure could not be read during the course of the experiment, but instead was taken before the discharge was initiated and again after the run was completed. The Torr metal was calibrated periodically over the range of pressures involved with the gases used to correct for alteration of sensitivity due to degradation of the vacuum transducer. For this purpose a Nester-Faust Hg gauge, reading from 10^{-4} to 15 Torr, was employed.

Procedure. For the 2-butene runs, the 2-butene was distilled into the reactant flask (a) equipped with a Teflon needle valve (b). Air was removed by several freeze–pump–thaw cycles using liquid nitrogen, valve (b) closed, and the assembly warmed to room temperature and weighed.

The assembly was then connected to the apparatus as in Figure 1 and evacuated. The mercury u-tube (for gas yield determination) in the vacuum line was isolated from the plasma reactor by means of a stopcock, since most experiments were to be carried out in the absence of mercury vapor. The 2-butene container was immersed in a dry ice–acetone bath (to facilitate flow rate control by lowering its vapor pressure), and liquid nitrogen was placed on the traps. A steady flow rate of 2-butene was established (as determined by a constant pressure reading on the torr meter) for a measured period of time, by partially opening valve b. If carrier gas was to be used, this was admitted via c and the total pressure measured. The discharge was then initiated by turning on the rf power. After a specified period of time (usually 30–60 min), the power was turned off and the pressure again measured (the time during which the flow was continued with no power was monitored), and the flow of gases stopped. The pressure was taken as the average of these two values (usually they were identical).

A standard mercury u-tube was then opened to the apparatus and the whole system isolated from the vacuum pump. The traps were allowed to warm to room temperature and the condensable gases collected by immersing a gas sample tube in liquid nitrogen. The quantity of gas formed was measured with the calibrated vacuum line. If possible, the gas was expanded until it occupied a pressure of ca. 1 atm in the gas tube. If the quantity of gas was too small for this, it was brought up to 1 atm with inert gas (nitrogen or helium). This was done to facilitate sampling and to insure a representative sample.

The traps were weighed in order to determine any nonvolatile residue, and the reactant vessel a was allowed to warm to room temperature and weighed in order to determine the amount of 2-butene passed. Polymers, when formed, were always in the reaction chamber itself and (when not too intractable) were extracted with $CHCl_3$ and weighed.

Analysis of Products. Little time was spent analyzing the (usually) small liquid fraction. NMR and ir indicated it to be a mixture of olefinic hydrocarbons. The small amount of polymer was not examined due to its intractibility.

Ir of the gas mixture produced in high-conversion runs showed an obvious absorption for acetylene (3300 cm^{-1}) and bands typical of olefinic hydrocarbons, but there were no significant, sharp absorptions at 1000 and 1800 cm^{-1} which are present in butadiene. The ir of the gases from low-conversion runs looked very similar to that of starting material.

Gas chromatography analysis of the gas mixture was achieved with two separate columns. Column 1 was ⅜ in. × 15 ft, 30% squalene on 60/80 Chromasorb P, and column 2 was ⅜ in. × 12 ft, 30% $\beta\beta'$ oxydipropionitrile on Chromasorb P. The order of product elution was very different on the two columns, and both were capable of separating *cis*- and *trans*-2-butene. Since the squalene column was better for that purpose, the yields were determined with it, although both columns give yields which are the same within experimental error.

Qualitative analysis was achieved by coinjection of authentic samples of individual gases and product mixtures on both columns. In this way the absence of significant amounts of isobutylene was conformed, as well as the presence of the products listed in Tables I, II, and III.

Quantitation was accomplished by photocopying the gas chromatography trace and weighing the peaks. No correction was made for the differing thermal conductivities in the few cases where the thermal conductivity detector was used. The areas of the peaks obtained with the flame ionization detector, however, was corrected for the carbon number of the product (area × 1/number of carbons). Several mixtures were analyzed with both detection systems and the results were the same within ±5%.

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Simulation and Evaluation of Chemical Synthesis. Congestion: a Conformation-Dependent Function of Steric Environment at a Reaction Center. Application with Torsional Terms to Stereoselectivity of Nucleophilic Additions to Ketones[1a]

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Abstract: An empirical, conformation-dependent function, related to congestion at a reaction center, is derived. Based upon calculating the surface area of cones of access defined by each hindering atom, the congestions calculated from three-dimensional models of 52 ketones were correlated with stereoselectivity of steric approach controlled nucleophilic addition reactions. For hydride reductions which were not steric approach controlled, addition of an empirical transition state again afforded good correlation correction with experimental stereoselectivity. It is proposed that the present function permits "factoring out" the steric effect for ketone addition reactions, and that it may also be useful in evaluating different conformations. An example of the latter is illustrated with 2-methylcyclopentanone. The mechanism of nucleophilic attack on ketones is discussed. The concept of a torsional effect is strongly supported by our results.

The most challenging problems for the synthetic organic chemist are generally those which involve stereoselective transformations. A large number of empirical rules have been formulated to aid the chemist in this regard.[2] Unfortunately such rules are often very specific with respect to the class of compounds to which they apply; furthermore, they are not always well grounded mechanistically. Orbital symmetry rules[3] have elegantly rationalized many selective transformations, but application to large polyfunctionalized molecules of synthetic interest is not always straightforward in the absence of detailed molecular orbital calculations.

While the synthetic chemist can usually look at a Dreiding model of a compound and predict which side of a reactive center is more "sterically hindered" to attack by a reagent, there has been no simple method of quantifying the chemist's perception. We have addressed the task of formulating the organic chemist's stereochemical rules in forms amenable for computer analysis of synthesis.[4,5]

Many stereochemical properties of molecules are independent of conformation (e.g., cis–trans relationships in rings), and may be perceived symbolically and manipulated algebraically.[6] Other conformation-dependent stereochemical relationships, e.g., axial-equatorial, group proximity, least hindered side, require, in general, evaluation of a three-dimensional molecular model. The models utilized in this paper were built by computer from two-dimensional structural diagrams with stereochemistry designated using the SYMIN module,[5-7] an interactive Westheimer type molecular mechanics[8] program.

Steric Control of Reactions. While steric hindrance is well