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Kinetics of the Stereospecific Photochemical Cyclodimerization of 2-Butene in the Liquid Phase[1a]

H. Yamazaki,[1b] R. J. Cvetanović,* and R. S. Irwin

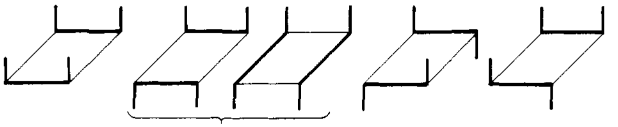
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

Received August 26, 1975

Abstract: Stereoselective photochemical cyclodimerization of liquid 2-butene, recently observed in this laboratory, has been investigated in greater detail. Particular attention has been paid to the kinetics of the cyclodimerization, which occurs with retention of geometric configuration in both 2-butene molecules incorporated into the cyclodimer. In mixtures of *trans*- and *cis*-2-butene, the distribution of the four isomers of the cyclodimer (1,2,3,4-tetramethylcyclobutane) undergoes characteristic drastic changes as the ratio of the two olefins is varied. The experimentally observed distribution of the four isomers as a function of the cis/trans ratio in the liquid 2-butene can be quantitatively reproduced by calculations based on theoretical rate expressions derived from a reaction mechanism which considers the statistical probability of encounters between the electronically excited and the ground-state *cis*- and *trans*-2-butene molecules. The effects of variation of the wavelength and the temperature on the extent of cyclodimerization in liquid 2-butene relative to its isomerization, acyclic dimerization, and photolytic fragmentation (followed by free radical reactions) have been investigated. At higher temperature and especially at shorter wavelengths, the extent of acyclic dimerization and photolysis tends to be enhanced. At 184.9 nm acyclic dimerization and photolytic processes predominate, and only relatively little cyclodimerization takes place. At 213.9 nm some cyclodimerization is observed even in the gas phase, especially at higher pressures, but its extent is very much smaller than in the liquid phase. No cyclodimerization is observed in the gas-phase triplet mercury, Hg 6($^3P_1$), photosensitized reaction. Quantitative data have been obtained on the very rapid reduction in the extent of photochemical cyclodimerization of liquid 2-butene as a result of dilution with isopentane.

Introduction

In a previous communication[2] from this laboratory, it was reported briefly that photochemical cyclodimerization of liquid 2-butene takes place with retention of geometric configuration in both 2-butene molecules which become incorporated in the cyclodimer. This can be represented schematically by the structural diagrams of the four 1,2,3,4-tetramethylcyclobutane isomers formed, in which the original two 2-butene fragments are indicated by heavier lines.



A (cis,cis,cis) B (cis,trans,cis) C (trans,trans,trans) D (cis,cis,trans)

It is evident that if the cyclodimerization is to occur with complete retention of configuration, pure *cis*-2-butene would have to form only A and B, pure *trans*-2-butene only B and C, while the remaining isomer D could be formed only in mixtures of *cis*- and *trans*-2-butene (in addition to A, B, and C). Such a remarkable selective formation of the four isomers is actually observed.[2]

Photochemical cyclodimerizations leading to the formation of cyclobutane ring compounds are frequently observed. They have received much attention in organic photochemistry,[3-5] more recently from the point of view of conservation of orbital symmetry, as well as in photobiology.[6-8] Photochemical cyclodimerization of liquid tetramethylethylene to octamethylcyclobutane has also been recently reported,[9,10] although it is, of course, not possible in this case to establish whether or not the process occurs with retention of configuration. Observation of complete retention of configuration in the photochemical cyclodimerization of liquid 2-butene provides, therefore, new insight into the mechanism of some of these photochemical processes. Moreover, studies of photochemical cyclodimerization to cyclobutane

Table I. Percentage Yields of the Four Tetramethylcyclobutane Isomers (A, B, C, D)[a] Formed in Photochemical Cyclodimerization of Liquid 2-Butene at Different Molar Fractions (X) of *trans*-2-Butene [X = trans/(cis + trans)][b]

	25 °C, Zn lamp				−78 °C, Zn lamp				−78 °C, Cd lamp			
X	A (%)	B (%)	C (%)	D (%)	A (%)	B (%)	C (%)	D (%)	A (%)	B (%)	C (%)	D (%)
0	52.3	43.9	0.8	2.9	54.4	41.7	0.5	3.4	56.6	39.4	0.6	3.4
	(54.4)	(45.6)	(0)	(0)	(56.6)	(43.4)	(0)	(0)	(59.0)	(41.0)	(0)	(0)
0.17	41.8	37.2	0.9	20.0	36.2	30.0	2.5	31.3	34.9	26.2	3.0	35.9
	(43.4)	(38.6)	(0.1)	(17.9)	(37.6)	(31.1)	(2.1)	(29.2)	(36.2)	(27.2)	(2.5)	(34.1)
0.33	31.3	29.4	3.7	35.6	21.7	23.0	8.6	46.7	18.6	18.7	10.7	52.0
	(32.4)	(30.5)	(3.0)	(34.1)	(22.5)	(23.8)	(8.4)	(45.3)	(19.2)	(19.3)	(10.4)	(51.1)
0.50	20.1	23.6	10.2	46.2	12.2	20.7	18.3	48.9	8.4	18.0	21.9	51.8
	(20.8)	(24.4)	(9.7)	(45.1)	(12.6)	(21.3)	(18.4)	(47.7)	(8.6)	(18.5)	(21.9)	(51.0)
0.67	9.6	23.9	20.9	45.5	3.8	23.9	32.5	39.9	3.3	22.2	33.9	40.7
	(9.9)	(24.7)	(20.8)	(44.5)	(3.9)	(24.6)	(32.9)	(38.6)	(3.4)	(22.7)	(34.1)	(39.8)
0.83	2.4	30.3	36.1	31.1	0.8	30.3	45.7	23.2	1.0	27.8	48.4	22.8
	(2.5)	(31.3)	(36.4)	(29.8)	(0.8)	(31.1)	(46.5)	(21.6)	(1.0)	(28.4)	(48.8)	(21.8)
1	0	42.2	55.6	2.2	0.5	38.1	59.4	2.0	0	35.8	63.0	1.2
	(0)	(43.5)	(56.5)	(0)	(0)	(39.3)	(60.7)	(0)	(0)	(36.5)	(63.5)	(0)

[a] A = cis, cis, cis; B = cis, trans, cis; C = trans, trans, trans; D = cis, cis, trans. [b] The values in parentheses are the "corrected" values, as explained in the text.

ring compounds generally do not include detailed kinetic information, perhaps mainly because of the appreciable complexity of the molecules involved. In constrast to this, the 2-butene system is sufficiently simple to lend itself readily to a detailed kinetic analysis. For these reasons, a more detailed and more complete study of the photochemical cyclodimerization of 2-butene has been carried out, with particular emphasis on the kinetics of cyclodimerization. The results are reported in the present paper.

Experimental Section

Irradiations of liquid 2-butene at room temperature were carried out in flat quartz reaction vessels 5-cm long, 1-cm wide, and about 1-mm deep. The shallow reaction vessel used for experiments at −78 °C was built-in into the bottom part of a Dewar flask and was irradiated from below through two quartz windows separated by vacuum. The temperature was maintained at −78 °C with dry ice-acetone slurry in the Dewar. The reaction vessel itself was 3.2 cm in diameter and was filled with a layer of olefin which covered the quartz window to a depth of about 1 mm. The vessel was connected to a mercury-free vacuum system. Gas-phase experiments were carried out in conventional cylindrical reaction vessels 5-cm i.d., 10 cm long.

Liquid 2-butene was irradiated with a Philips 93107E cadmium lamp, a 93106E zinc lamp, or with a low-pressure mercury resonance lamp (for experiments at 184.9 nm). Direct photolysis in the gas phase at 213.9 nm was carried out with Philips 93106E zinc lamp, and the gas-phase triplet mercury [Hg $6(^3P_1)$] photosensitized experiments were done with the low-pressure mercury resonance lamp, taking precaution to filter out the 184.9-nm resonance line by a cut-off glass filter (Corning 9-54).

Analysis of the products was carried out on a combined gas chromatographic apparatus, which simultaneously fed aliquots into three different columns: a 300-ft squalane capillary column at room temperature, a 300-ft dinonyl phthalate capillary column at 0 °C, and a 20-ft packed squalane modified alumina column at room temperature. Helium carrier gas and hydrogen-flame detectors were used with all three columns. Quantitative determinations of the yields were based on peak area measurements and calibrations with standard samples. Hydrogen-flame detector responses proportional to the number of carbon atoms in the molecules were assumed.

Identities of the hydrocarbon products were established in a number of ways. The procedure used and the evidence obtained for the identity of the four 1,2,3,4-tetramethylcyclobutane isomers has been described in the earlier communication.[2] For other products, similar methods were employed. These included the use of a simple correlation between the retention times on the squalane capillary column and the boiling points of the hydrocarbons, a gas chromatograph-mass spectrometer (Atlas CH4) combination to obtain mass spectra of compounds eluted from the capillary columns, seeding with authentic samples when available, and producing the suspected products by various photochemical reactions and comparing their chromatograms with those of the unknown products. Other analytical techniques, such as ir, NMR, and mass spectrometry, have also been used, as described in the first communication.[2]

In the experiments with liquid 2-butene, irradiations were generally 18 h. The conversion of 2-butene was of the order of 0.2%. Irradiation times in the gas-phase experiments were of the order of 2-4 h.

The *cis*- and *trans*-2-butene and isopentane used in the experiments were Phillips Petroleum Co. research grade products and were used without further purification, but after thorough outgassing.

Results

Percentage Yields of the Cyclodimer Isomers. The percentage yields of the four 1,2,3,4-tetramethylcyclobutane isomers (A, B, C, and D), formed at different ratios of *trans*- and *cis*-2-butene, are shown in Table I. X represents the molar fraction of *trans*-2-butene in the condensed 2-butene. Three series of experiments were carried out: (1) at 25 °C with a Zn lamp as the light source, (2) at −78 °C with a Zn lamp, and (3) at −78 °C with a Cd lamp.

It can be seen that, with pure *cis*-2-butene (i.e., at $X = 0$), A and B are essentially the only isomers formed. Similarly, with pure *trans*-2-butene ($X = 1$) there is almost exclusive formation of B and C. As the fraction of *trans*-2-butene increases from 0 to 1, the amount of A continuously decreases to negligible amounts, the amount of C continuously increases, B goes through a minimum corresponding roughly to equimolar mixtures of *cis*- and *trans*-2-butene ($X = 0.5$), and D goes simultaneously through a maximum, declining again to negligible amounts at $X = 1$. The behavior is qualitatively very much the same in the three series, although there are some quantitative differences which will be discussed later. The values in parentheses are the "corrected" percentage yields at each value of X after allowing for very small amounts of nonstereoselective formation of C and D in pure *cis*- and of D in pure *trans*-2-butene. These corrections are very minor and have been made approximately by subtracting from the observed yields of D the amounts (of 2 to 3%) formed at $X = 0$ and 1 (and interpolating the required corrections linearly for the intermediate values of X). The yields of C were corrected by subtracting uniformly from all the values in each series the small yield (0.5-0.8%) found for C at $X = 0$. No corrections of the yields of A were made except that the yield of 0.5% at $X = 1$ in the −78 °C series with the zinc lamp (in contrast to the negligible yields of A at $X = 1$ in the other two series) was

Table II. Yields of the C_8 Products Other Than Tetramethylcyclobutane Relative to the Total Yield of the Four Isomers of 1,2,3,4-Tetramethylcyclobutane from Liquid 2-Butene Irradiated at the Indicated Wavelength (λ), Temperature (Temp), and Molar Fractions of *trans*-2-Butene (X)[a]

			Dienes[a]								Alkenes[b]							Para-ffin[c]
				$M_1 \cdot M_2$			$M_2 \cdot M_2$					$M_2 \cdot sB$			$V \cdot sB$			
λ, nm	Temp, °C	X	$M_1 \cdot M_1$	t	c	Tot	tt	tc	cc	Tot	$M_1 \cdot sB$	t	c	Tot	t	c	Tot	sB·sB
Cd lamp (214.4 nm)	−78	0			0.007	0.007			Tr	Tr	0.060	0.003	0.043	0.046	0.024	0.052	0.076	0.012
		0.17			0.006	0.006		0.008	Tr	0.008	0.054	0.009	0.045	0.054	0.028	0.050	0.078	0.008
		0.33			0.005	0.005	Tr	0.012	Tr	0.012	0.057	0.019	0.040	0.059	0.032	0.041	0.073	0.012
		0.50			0.004	0.004	Tr	0.003	0.003	0.006	0.063	0.027	0.031	0.058	0.030	0.036	0.066	0.015
		0.67			0.005	0.005	0.004	0.007	Tr	0.011	0.053	0.038	0.020	0.058	0.033	0.033	0.066	0.011
		0.83			0.004	0.004	0.007	Tr		0.007	0.036	0.050	0.012	0.062	0.031	0.022	0.053	0.014
		1.00					0.009	Tr	Tr	0.009	0.030	0.057		0.057	0.029	0.013	0.042	0.011
213.9	−78	0	0.012		0.021	0.021	Tr	0.002	0.014	0.016	0.094	0.002	0.123	0.125	0.036	0.055	0.091	0.004
		0.17	0.011		0.018	0.018	Tr	0.005	0.008	0.013	0.091	0.020	0.112	0.132	0.043	0.051	0.094	0.006
		0.33	0.005		0.020	0.020	Tr	0.009	0.009	0.018	0.102	0.053	0.099	0.152	0.034	0.052	0.086	Tr
		0.50	0.006		0.017	0.017	0.002	0.009	0.003	0.014	0.096	0.062	0.076	0.138	0.036	0.046	0.082	0.024
		0.67	0.008		0.005	0.005	0.005	0.006	0.002	0.013	0.068	0.085	0.049	0.134	0.039	0.038	0.077	0.005
		0.83	0.010		0.007	0.007	0.008	0.006	0.002	0.016	0.058	0.103	0.025	0.128	0.041	0.033	0.074	0.007
		1.00	0.008		0.002	0.002	0.011	0.002		0.013	0.048	0.127	0.003	0.130	0.039	0.028	0.067	0.004
213.9	25	0	0.025	0.049	0.029	0.078	0.010	0.017	0.010	0.037	0.044	0.005	0.031	0.036	0.013	0.076	0.089	0.017
		0.17	0.030	0.024	0.010	0.034	0.014	0.021	0.008	0.043	n.d.	0.009	0.032	0.041	0.017	0.069	0.086	0.032
		0.33	0.028	0.044	0.027	0.071	0.014	0.020	0.010	0.044	0.041	0.019	0.033	0.052	0.026	0.065	0.091	0.027
		0.50	0.046	0.079	0.037	0.116	0.026	0.037	0.009	0.072	0.066	0.050	0.042	0.092	0.038	0.071	0.109	0.048
		0.67	0.040	0.052	0.034	0.086	0.022	0.026	0.010	0.058	0.066	0.063	0.024	0.087	0.052	0.052	0.104	0.057
		0.83	0.048	n.d.	0.034	n.d.	0.031	0.035	0.009	0.075	0.067	0.091	0.023	0.114	0.064	0.039	0.103	0.077
		1.00	0.058	0.083	0.032	0.115	0.046	0.029	0.009	0.084	0.068	0.154	0.014	0.168	0.082	0.021	0.103	0.106
184.9	−78	0	0.83	0.03	2.04	2.07	0.12		1.32	1.44	3.36	0.17	4.72	4.89		0.124	0.124	0.361
	25	0	1.09	0.60	1.82	2.42	0.16	0.58	1.00	1.74	1.83	0.29	2.01	2.30	0.034	0.109	0.143	0.631
	−78	1.00	0.76	1.32	0.09	1.41	1.34			1.34	2.72	4.17	0.15	4.32	0.412	0.102	0.514	0.693

[a] M_1, $CH_3\dot{C}HCH{=}CH_2$; M_2, $CH_3CH{=}CH\dot{C}H_2$; V, $CH_2\dot{C}{=}CHCH_3$; sB, $CH_3CHCH_2CH_3$; t, trans; c, cis; Tot, total; tt, trans, trans; tc, trans, cis; cc, cis, cis; Tr, trace; n.d., not determined. $M_1 \cdot M_1$, 3,4-dimethyl-1,5-hexadiene; $M_1 \cdot M_2$, 3-methyl-1,5-heptadiene; $M_2 \cdot M_2$, 2,6-octadiene. [b] $M_1 \cdot sB$, 3,4-dimethyl-1-hexene; $M_2 \cdot sB$, 5-methyl-2-heptene; V·sB, 3,4-dimethyl-2-hexene. [c] sB·sB, 3,4-dimethylhexane.

Table III. Products of the Photolysis of 2-Butene in the Gas Phase at 25 °C and Comparison with the Photolysis of Liquid 2-Butene at 25 °C.[a, b]

		Photolysis at 213.9 nm						Hg 6($^3P_1$) photosensitization			
Experiment number		1	2	3	4	5	6	7	8	9	10
Butene reactant		Cis	Cis	Cis	Cis	Trans	Trans	Cis	Cis	Trans	Butene-1
Pressure (Torr)		583	1483	1493	Liquid	1492	Liquid	1230	1180	1177	1178
Irradiation (h)		3	1	3	18	3	18	3	4	4	4
r_i (μmol/h)		6.32	18.85	11.94	22.74	2.87	*c*	36.88	*d*	*d*	*d*
Propane		0.1	1.0	0.4			0.02	0.04	n.d.		0.02
Propene		2.2	0.5	0.08	0.09	1.9	0.02	0.21	n.d.	0.09	0.05
n-Butane		0.2	0.4	0.6	0.09	1.9	0.21	0.82	n.d.	0.68	0.33
Butene-1		17.0	27.7	19.8	23.6	n.d.	n.d.	5.2	n.d.	n.d.	n.d.
trans-2-Butene		100	100	100	100			100	n.d.		
cis-2-Butene						100					
$M_1 \cdot Al$[e]		0.88	0.13	0.25		1.32		0.07	0.06	0.06	0.55
$M_2 \cdot Al$[e]	trans	0.71	0.09	0.19		1.07		0.05	0.04	0.06	0.48
	cis	0.53	0.07	0.14		0.70		0.05	0.04	0.03	0.37
$sB \cdot Al$[e]		1.66	0.24	0.40		2.33		0.15	0.13	0.14	0.59
$M_1 \cdot M_1$[f]		0.55	0.15	0.28	0.15	0.87	0.16	0.37	0.36	0.34	0.15
$M_1 \cdot M_2$[f]	trans	0.67	0.23	0.33	0.29	1.20	0.16	0.42	0.41	0.46	0.23
	cis	0.51	0.13	0.24	0.17	0.67	0.06	0.40	0.37	0.23	0.14
$M_2 \cdot M_2$[f]	trans,trans	0.27	0.06	0.12	0.06	0.46	0.09	0.13	0.14	0.21	0.08
	trans,trans	0.40	0.05	0.17	0.10	0.61	0.06	0.25	0.25	0.23	0.11
	cis,cis	0.14	0.04	0.05	0.06	0.17	0.02	0.18	0.12	0.05	0.04
$M_1 \cdot sB$[g]		1.77	0.47	0.62	0.29	2.38	0.17	1.14	0.96	1.09	0.32
$M_2 \cdot sB$[g]	trans	1.15	0.25	0.41	0.03	1.76	0.29	0.72	0.73	0.89	0.26
	cis	0.91	0.18	0.31	0.18	1.15	0.08	0.72	0.70	0.47	0.16
$V \cdot sB$[g]	trans				0.07		0.16				
	cis				0.45		0.04				
$sB \cdot sB$[h]		0.94	0.20	0.30	0.10	1.41	0.20	0.64	0.62	0.66	0.11
A[i]		0.028	0.067	0.10	3.10						
B[i]		0.068	0.063	0.11	2.60	0.073	0.80				
C[i]					0.04		1.08				
D[i]					0.17		0.04				

[a] The yields are expressed relative to the yield of the geometric isomer, r_i, taken as 100. r_i was directly measured, when feasible, or was estimated by comparison, as indicated in the Table and discussed in the text. [b] n.d., not determined; Al, allyl; M_1, $CH_3\dot{C}HCH{=}CH_2$; M_2, $CH_3CH{=}CH\dot{C}H_2$; sB, $CH_3\dot{C}HCH_2CH_3$; V, $CH_3CH{=}\dot{C}CH_3$. [c] Assumed to be the same as in 4. [d] Assumed to be the same as in 7. [e] $M_1 \cdot Al$, 3-methyl-1,5-hexadiene; $M_2 \cdot Al$, 1,5-heptadiene; $sB \cdot Al$, 4-methyl-1-hexene. [f] $M_1 \cdot M_1$, 3,4-dimethyl-1,5-hexadiene; $M_1 \cdot M_2$, 3-methyl-1,5-heptadiene; $M_2 \cdot M_2$, 2,6-octadiene. [g] $M_1 \cdot sB$, 3,4-dimethyl-1-hexene; $M_2 \cdot sB$, 5-methyl-2-heptene; $V \cdot sB$, 3,4-dimethyl-2-hexene. [h] $sB \cdot sB$, 3,4-dimethylhexane. [i] Isomers of 1,2,3,4-tetramethylcyclobutane.

neglected. After these corrections, the yields were again normalized to 100%, and the normalized values are shown in Table I (in parentheses). The corrections were made in order to allow for a very minor nonselective reaction path and, thus, obtain a more appropriate input for the kinetic analysis of the stereoselective cyclodimerization, which will be given in the next section.

In comparing the results at −78 °C with the Zn lamp with those obtained with the Cd lamp, it should be remembered that the extinction coefficient of 2-butene at the intense 228.8-nm line from the Cd lamp is much smaller than at the considerably weaker 214.4-nm line. It is therefore possible (although quantitative evaluations cannot be made) that the weak 214.4-nm line was mainly responsible for the photochemical reactions with the Cd lamp. Some support for this view was obtained with and without a nickel sulfate filter, which was shown to absorb strongly the 214.4-nm Cd line but transmits the 228.8- and 226.5-nm lines. Only an extremely small amount of reaction products was observed when the nickel sulfate filter was used. It appears, therefore, very likely that the 214.4-nm line was indeed responsible for the photochemical reactions observed in liquid 2-butene with the Cd lamp.

Products Other Than Cyclodimers. Besides the four cyclodimer isomers formed, a certain amount of other C_8 products is invariably observed. Most of these products result from some photolysis of 2-butene to give mainly methallyl radicals (two resonance forms) and H atoms. The latter add to 2-butene to form *sec*-butyl radicals. These radicals combine to form a number of C_8 dienes, alkenes, and a paraffin (3,4-dimethylhexane). One of the alkenes, 3,4-dimethyl-2-hexene, incorporates a *sec*-butyl and a vinylic $CH_3\dot{C}{=}CHCH_3$ radical, but is probably formed by molecular rearrangement of the "hot" cyclodimer rather than by free radical combination, as will be pointed out later. Table II shows the yields of these products expressed relative to the total yield of cyclodimer (the sum of A, B, C, and D).

It can be seen that, in the photolysis of liquid 2-butene with Cd and Zn lamps, these products represent some 20–60% of the extent of cyclodimerization. They are produced least with the Cd lamp, increase somewhat with the Zn lamp at −78 °C, and even more at 25 °C, and become very extensive at 184.9 nm. In fact, at this last wavelength only small amounts of A, B, C, and D are observed, and the very complex products have not been fully analyzed and identified. The results at 184.9 nm will, therefore, be only briefly mentioned, without attempting to discuss the reaction mechanism.

As reported previously,[2] the main reaction path in the photolysis of liquid 2-butene is cis-trans isomerization. Smaller amounts of 1-butene and probably of methylcyclopropane (not definitely identified) are also formed. (Yields of 1-butene in the photolysis of liquid 2-butene, reported further below, include any methylcyclopropane present.)

Comparison with Gas-Phase Photolysis at 213.9 nm and Triplet Mercury Photosensitization at 253.7 nm. For comparison with the results obtained with liquid 2-butene, several direct photolytic experiments were carried out in the gas phase at 213.9 nm and also the triplet mercury, Hg 6($^3P_1$) photosensitized reaction, also in the gas phase. The results of interest are shown in Table III. The yields are ex-

Table IV. Effect of Dilution with Isopentane on the Products of Irradiation of Liquid *cis*-2-butene with Zn Lamp at 25 °C

cis-2-Butene (μM)		11337	5387	3608	2734	2416	2120
Isopentane (μM)		0	5385	7096	8008	8550	8708
Isopentane/*cis*-2-butene		0	1.00	1.97	2.93	3.54	4.11
Irradiation (h)		5	2	16.5	18	20	22.5
trans-2-Butene (μM/h)		6.06	4.26	6.21	7.22	5.83	6.94
		Yields of products relative to *trans*-2-butene taken as 100					
A[a]		1.68	0.500	0.264	0.199	0.185	0.155
B[a]		1.37	0.306	0.216	0.159	0.141	0.127
D[a]		0.100	0.028	0.029	0.031	0.025	0.029
$M_1 \cdot M_1$[a]		0.056	0.022	0.033	0.030	0.032	0.025
$M_1 \cdot M_2$[a]	trans	0.097	0.112	0.028	0.020	0.022	0.016
	cis	0.115	0.060	0.048	0.037	0.041	0.035
	Total	0.212	0.172	0.076	0.057	0.063	0.051
$M_2 \cdot M_2$[a]	trans,trans	0.006		0.007	0.005	0.006	0.005
	trans,cis	0.038	0.004	0.022	0.019	0.020	0.016
	cis,cis	0.035	0.013	0.012	0.010	0.011	0.010
	Total	0.079	0.017	0.041	0.034	0.037	0.031
$M_1 \cdot sB$[a]		0.240	0.079	0.065	0.058	0.058	0.048
$M_2 \cdot sB$[a]	trans	0.015	0.010	0.010	0.009	0.010	0.007
	cis	0.110	0.051	0.035	0.027	0.030	0.013
	Total	0.125	0.061	0.045	0.036	0.040	0.020
$V \cdot sB$[a]	trans	0.091	0.024	0.017	0.014	0.011	0.007
	cis	0.203	0.075	0.020	0.020	0.013	0.009
	Total	0.294	0.099	0.037	0.034	0.024	0.016
$sB \cdot sB$[a]		0.047	0.027	0.023	0.024	0.023	0.019

[a] The symbols used for the products have the same meaning as in Tables II and III.

pressed relative to the yield of the geometric isomer of the 2-butene studied taken as 100, since this should be directly proportional to the number of quanta absorbed. In some cases, however, the rates of geometric isomerization had to be estimated approximately by analogy, as indicated in Table III, since direct measurements were not feasible. The last column in Table III gives some data for 1-butene because it forms some of the same products as 2-butene. Geometric isomerization is of course not observed in the case of 1-butene, and in order to obtain a basis for at least a rough comparison with other experiments in Table III, the yields of the 1-butene products are expressed relative to the yield of *trans*-2-butene in the mercury photosensitized reaction of *cis*-2-butene under comparable conditions.

It is evident from Table III that even in the gas-phase photolysis of 2-butene at 213.9 nm some 1,2,3,4-tetramethylcyclobutane is formed. However, the rates of its formation relative to the rate of isomerization are extremely small, although they seem to show an appreciable increase when the pressure is substantially raised. *cis*-2-Butene forms only A and B, i.e., the same two isomers as in the liquid phase. One experiment carried out with *trans*-2-butene showed B as the only isomer of the cyclodimer while both B and C are formed in the liquid phase. Photolysis is clearly much more extensive in the gas-phase experiments. Furthermore, gas-phase photolysis leads not only to CH rupture but also to CC rupture in butene molecules, as evidenced by the substantial yields of C_7 products (3-methyl-1,5-hexadiene, 1,5-heptadiene, and 4-methyl-1-hexene), which can be explained by combination of allyl radicals with methallyl and *sec*-butyl radicals. The data in Table III show that these products are not formed in the liquid-phase irradiation of 2-butene.

Mercury photosensitized reaction, which must proceed via an intermediate electronically excited butene molecule in the triplet state, does not produce any 1,2,3,4-tetramethylcyclobutane. The observed products are such as would be expected from free radical reactions (involving, in particular, methallyl and *sec*-butyl radicals, as well as a smaller amount of allyl radicals). These products will not be further discussed here, except to say that they have, together with the products from a number of other mercury photosensitized reactions of simple olefins and diolefins, taken singly or in pairs, in the presence or absence of H_2, helped to confirm the identity of a number of products observed in the present study. (The procedure used, too lengthy to describe in detail here, involved the production of the same products by alternative reaction paths, calculation of their boiling points from their retention times on a squalane capillary column and comparison with the corresponding literature values, seeding with authentic samples when available, and in some cases synthesizing authentic samples. The GC-MS combination was also of assistance.)

Effect of Dilution with Isopentane on the Photochemical Cyclodimerization of Liquid *cis*-2-Butene. As reported briefly previously,[2] dilution with neopentane of liquid *cis*-2-butene at room temperature rapidly caused a drastic reduction in the yields of the cyclodimer isomers. This effect has now been investigated more quantitatively at room temperature with a Zn lamp and with isopentane as the diluent. The results obtained are summarized in Table IV. For each experiment the yields are given relative to *trans*-2-butene taken as 100. The yields of the cyclodimerization products (essentially only A and B) are drastically reduced even at relatively moderate dilution with isopentane. The effect on the main reaction path, isomerization to *trans*-2-butene, on the other hand is negligible within the experimental scatter due to fluctuations of the light source. It is very significant that, although the yields of the cyclodimers rapidly decrease with dilution, their distribution remains constant. (A slight increase in the fraction of D at large dilutions is explainable by the substantial formation of *trans*-2-butene at the long exposures which had to be used.) These and other results will be discussed in the next section.

Discussion

Kinetics of Cyclodimerization. The results of the present and previous[2] study show that the photochemical cyclodimerization of liquid 2-butene occurs stereoselectively, i.e., with complete retention of configuration of both 2-butene fragments which form the dimer, even though the latter may possess initially more than 100 kcal/mol excess energy. Such behavior is consistent only with a "concerted" cycloaddition, i.e., without intermediate formation of 1,4-

biradicals of appreciable lifetime, which would permit geometric randomization. Furthermore, the 2-butene molecule, which has absorbed a photon (and, thus, as much as 134 kcal/mol of energy at 213.9 nm and 155 kcal/mol at 184.9 nm), must retain its own geometric configuration until the formation of cyclodimer is completed. Initial formation of an electronically excited 2-butene molecule in the singlet state (the Franck-Condon $\pi\pi^*$ singlet[9] or, perhaps more probably, at least at 213.9 nm, the first Rydberg singlet[11,12]) must therefore be invoked. Mercury photosensitized reaction (Table III) shows that the electronically excited triplet 2-butene does not add to any appreciable extent to other 2-butene molecules. It undergoes preferential geometric isomerization and deactivation to the ground state and, to a considerably smaller extent at the pressures used, fragmentation, which takes places mainly through splitting of CH but also of some CC bonds. (The fragmentation is followed by free radical reactions, leading to the products indicated in Table III, which are obvious and need not be specified here explicitly.)

It is not possible at this time to state the detailed dynamics of the concerted cycloaddition step. In particular, it may only be speculated whether or not it proceeds via an electronically excited intermediate complex (exciplex) of finite lifetime. From a kinetic point of view, it may suffice to leave the matter of potential involvement of intermediate complexes open and to consider formally the cyclodimerization step simply as a binary reaction between an excited and an unexcited 2-butene molecule, as in the following reaction scheme (Cis and Tr stand for *cis*- and *trans*-2-butene, respectively; A, B, C, D are the four isomers of 1,2,3,4-tetramethylcyclobutane).

$$\mathrm{Cis} + h\nu \rightarrow \mathrm{Cis}^* \qquad (\mathrm{Iac})$$

$$\mathrm{Tr} + h\nu \rightarrow \mathrm{Tr}^* \qquad (\mathrm{Iat})$$

$$\mathrm{Cis}^* + \mathrm{Cis} \rightarrow \alpha\mathrm{A} + (1-\alpha)\mathrm{B} \qquad (k_{\mathrm{CC}})$$

$$\mathrm{Tr}^* + \mathrm{Tr} \rightarrow \beta\mathrm{C} + (1-\beta)\mathrm{B} \qquad (k_{\mathrm{TT}})$$

$$\mathrm{Cis}^* + \mathrm{Tr} \rightarrow \mathrm{D} \qquad (k_{\mathrm{CT}})$$

$$\mathrm{Tr}^* + \mathrm{Cis} \rightarrow \mathrm{D} \qquad (k_{\mathrm{TC}})$$

$$\mathrm{Cis}^* \ (+\ \mathrm{M}) \rightarrow \text{isomerization} \qquad (k_{\mathrm{Ci}})$$

$$\mathrm{Cis}^* \ (+\ \mathrm{M}) \rightarrow \text{fragmentation} \qquad (k_{\mathrm{Cf}})$$

$$\mathrm{Tr}^* \ (+\ \mathrm{M}) \rightarrow \text{isomerization} \qquad (k_{\mathrm{Ti}})$$

$$\mathrm{Tr}^* \ (+\ \mathrm{M}) \rightarrow \text{fragmentation} \qquad (k_{\mathrm{Tf}})$$

(An analogous reaction scheme with involvement of butene exciplexes can be similarly formulated.) M is introduced in the last four reactions to indicate involvement of collisions with neighboring molecules in deactiving Cis* and Tr* to ground-state molecules with concurrent geometric isomerization, the main reaction path.

Applying the steady-state treatment to [Cis*] and [Tr*] and writing $a = r_{\mathrm{A}}/r_{(\mathrm{A+B+C+D})}$, $b = r_{\mathrm{B}}/r_{(\mathrm{A+B+C+D})}$, $c = r_{\mathrm{c}}/r_{(\mathrm{A+B+C+D})}$, and $d = r_{\mathrm{D}}/r_{(\mathrm{A+B+C+D})}$, where r denotes rates of product formation, it can be shown that

$$a = \alpha \Big/ \left[1 + \omega\frac{X}{1-X} + \epsilon\left(\frac{X}{1-X}\right)^2 \right] \qquad (1)$$

$$c = a\frac{\epsilon\beta}{\alpha}\left(\frac{X}{1-X}\right)^2 \qquad (2)$$

$$b = \frac{1-\alpha}{\alpha}a + \frac{1-\beta}{\beta}c \qquad (3)$$

$$d = 1 - (a+b+c) \qquad (4)$$

where $X = (\mathrm{Tr})/(\mathrm{Cis}+\mathrm{Tr})$; $\epsilon = (\epsilon_{\mathrm{T}}/\epsilon_{\mathrm{C}})(k_{\mathrm{TT}}/k_{\mathrm{CC}})[(k_{\mathrm{Ci}} + k_{\mathrm{Cf}})/(k_{\mathrm{Ti}} + k_{\mathrm{Tf}})]$, $\omega = (k_{\mathrm{CT}}/k_{\mathrm{CC}}) + (k_{\mathrm{TC}}/k_{\mathrm{CC}})\epsilon$, and $\epsilon_{\mathrm{T}}/\epsilon_{\mathrm{C}}$ is the ratio of the extinction coefficients of *trans*- and *cis*-2-butene. In the derivation of these expressions, advantage was taken of the fact that in the present reaction system $(k_{\mathrm{Ci}} + k_{\mathrm{Cf}}) \gg k_{\mathrm{CC}}$, $(k_{\mathrm{Ci}} + k_{\mathrm{Cf}}) \gg |k_{\mathrm{CT}} - k_{\mathrm{CC}}|$ and similarly $(k_{\mathrm{Ti}} + k_{\mathrm{Tf}}) \gg k_{\mathrm{TT}}$ and $(k_{\mathrm{Ti}} + k_{\mathrm{Tf}}) \gg |k_{\mathrm{Tc}} - k_{\mathrm{TT}}|$. (A possible electronic energy transfer between Cis* and Tr and vice versa is not explicitly taken into account in the above reaction scheme. Its effect would be such to alter the effective value of ϵ.)

It is evident that the values of a, b, c, and d at different molar fractions of *trans*-2-butene (X) are completely determined by the values of four parameters: α, β, ϵ, and ω. However, two of these, α and β, are simply the fractions of A and C formed in pure *cis*- and pure *trans*-2-butene, respectively, and are, therefore, not "adjustable" parameters. ϵ is dependent on the ratio of the extinction coefficients of *trans*- and *cis*-2-butene, but depends also on $(k_{\mathrm{TT}}/k_{\mathrm{CC}})$ and $(k_{\mathrm{Ci}} + k_{\mathrm{Cf}})/(k_{\mathrm{Ti}} + k_{\mathrm{Tf}})$, both of which may be expected to be of the order of (although not necessarily exactly equal to) unity. Thus, ϵ is an "adjustable" parameter, as is also ω, which incorporates ϵ and also $(k_{\mathrm{CT}}/k_{\mathrm{CC}})$ and $(k_{\mathrm{TC}}/k_{\mathrm{CC}})$. Since the last two ratios should be of the order of unity, ω should be approximately $(1 + \epsilon)$.

Although ϵ and ω are adjustable parameters in the sense that they have to be adjusted in order to optimize the coincidence between the calculated and the experimental values of a, b, c, and d at all values of X, they can be approximately obtained from eq 1-4 for special values of X. Thus, it can be shown that for the point where $a = c$, i.e., at $X_{\mathrm{a=c}}$

$$\epsilon = (\alpha/\beta)[(1 - X_{\mathrm{a=c}})^2/X^2_{\mathrm{a=c}}] \qquad (5)$$

Similarly, at $X = 0.5$

$$\omega = (1+\epsilon)[d_{0.5}/(1 - d_{0.5})] \qquad (6)$$

where $d_{0.5}$ is the value of d at $X = 0.5$.

First approximations to ϵ and ω can be readily calculated from eq 5 and 6. They have then to be slightly adjusted so as to optimize the agreement with all experimental values. This procedure was used to compute (on a programmable desk calculator) the theoretical curves for a, b, c, and d as functions of X from the experimental values in Table I. The results of these computations are shown in Figure 1, in which the experimental points are the "corrected" values (the values in parentheses) from Table I, and the curves are the computed theoretical curves. The plots give the computed curves for the three series of experiments from Table I: 25 °C, Zn lamp (Figure 1a); −78 °C, Zn lamp (Figure 1b); and −78 °C, Cd lamp (Figure 1c). The optimized parameters used in the computations are summarized in Table V.

It can be seen from Figure 1 that the theoretical curves and the experimental points agree remarkably well in all three series. Minor deviations are well within the potential analytical errors. Although the "corrected" values from Table I were used in the computations, it should be mentioned that the differences between the corrected and the original percentages are very minor, and the original data could be used in the computations essentially equally successfully. The corrected fractions are nevertheless considered to be a more appropriate input for these computations because they factor out the small amount of randomized cycloaddition.

The values of the parameters listed in Table V should be viewed in comparison with an idealized case in which $\alpha = \beta = 0.5$, $\epsilon = 1$, and $\omega = 2$, i.e., the case of equal statistical probability between all analogous reactions of Cis* and Tr* (i.e., $k_{\mathrm{CC}} = k_{\mathrm{TT}} = k_{\mathrm{CT}} = k_{\mathrm{TC}}$ and $k_{\mathrm{Ci}} + k_{\mathrm{Cf}} = k_{\mathrm{Ti}} + k_{\mathrm{Tf}}$)

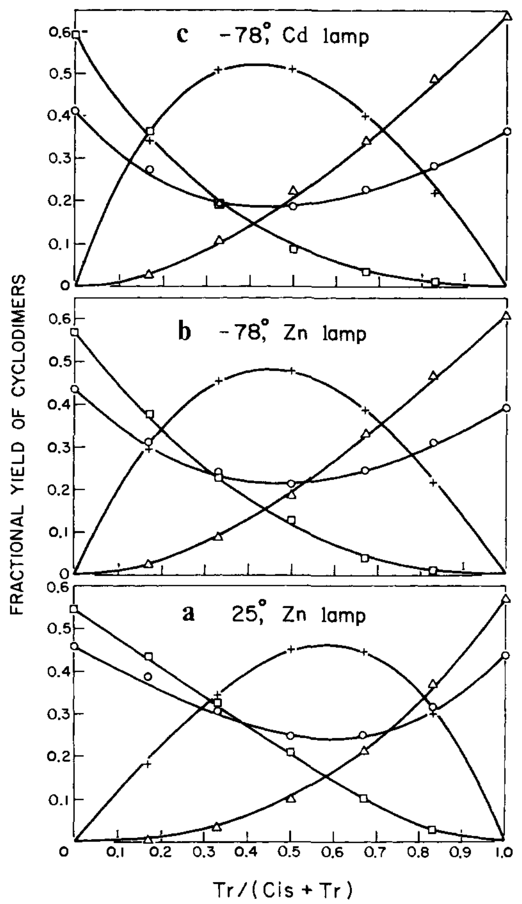


Figure 1. Fractional yields of the four cyclodimer isomers as a function of the molar fractions of *trans*-2-butene in liquid 2-butene: (a) experiments with Zn lamp at 25 °C; (b) experiments with Zn lamp at −78 °C; (c) experiments with Cd lamp at −78 °C. The points are the "corrected" fractional yields (based on the values in parentheses in Table I) for the four isomers: A (□), B (○), C (△), and D (+). The curves are the computed curves from the theoretical rate expressions, as explained in the text.

Table V. Parameters Used in the Computation of the Theoretical Curves of *a*, *b*, *c*, and *d* Plotted in Figure 1

Experimental series	α	β	ϵ	ω
25 °C, Zn lamp	0.544	0.565	0.50	1.20
−78 °C, Zn lamp	0.566	0.607	1.55	2.30
−78 °C, Cd lamp	0.590	0.635	1.90	3.00

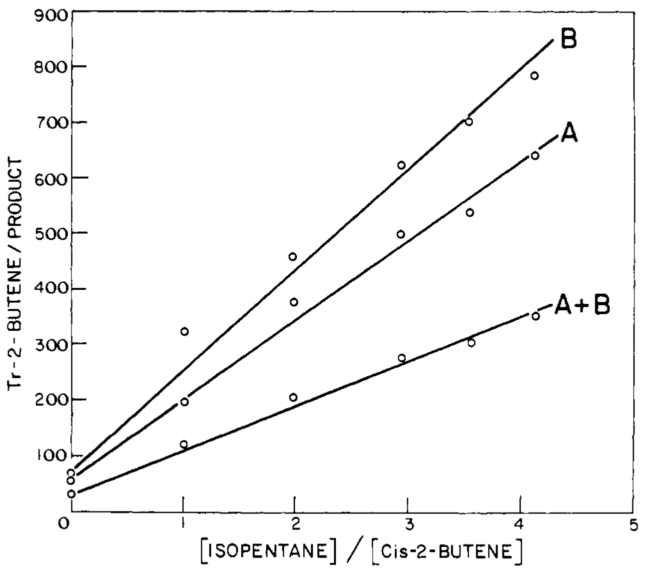


Figure 2. Effect of dilution on the yields of the cyclodimers: plot of eq 7 for A, B, and A + B.

and equal extinction coefficients of *trans*- and *cis*-2-butene (i.e., $\epsilon_T = \epsilon_C$). In this idealized case, the distribution of A, B, C, and D as a function of X would be perfectly symmetrical, with $a = b = 0.5$, $c = d = 0$ at $X = 0$; $c = b = 0.5$, $a = d = 0$ at $X = 1$; and $a = c = 0.125$, $b = 0.25$, and $d = 0.5$ at $X = 0.5$. Deviations from symmetry are caused by departures of the rates of reactions of Cis* and Tr* from statistical probability and by unequal extinction coefficients of *trans*- and *cis*-2-butene ($\epsilon_T \neq \epsilon_C$). Departure from statistical probability is immediately evident from results with pure *cis*- and pure *trans*-2-butene: a is not equal to b in the former case and c is not equal to b in the latter, i.e., $\alpha \neq 0.5$, $\beta \neq 0.5$. The exact reason for such departures, although they are not very pronounced, is not certain. They may perhaps be partly of steric origin. Inequality of ϵ_T and ϵ_C is strongly suggested by extrapolations of the existing gas-phase data at shorter wavelengths and by several gas-phase measurements which we have made in the wavelength region of interest. Our attempts to measure the extinction coefficients of neat liquid *trans*- and *cis*-2-butene at 214 nm at room temperature suggest that $\epsilon_C > \epsilon_T$, but the values may have been strongly influenced by an impurity, particularly in *cis*-2-butene, since successive distillations seemed to decrease the absorbance. How would the ratio of these values be affected by a decrease in temperature to −78 °C is uncertain. Since the parameter ϵ in the present work does not depend only on ϵ_T/ϵ_C but also on k_{TT}/k_{CC} and $(k_{Ci} + k_{Cf})/(k_{Ti} + k_{Tf})$ (as well as on any electronic energy transfer between Cis* and Tr and vice versa), its departures from unity and variations between the three experimental series (Table V) cannot be ascribed only to a variation in ϵ_T/ϵ_C. The derived values of ω (Table V) approach roughly $(1 + \epsilon)$, as expected in the ideal case. However, there are some departures even in this case, indicating some disparity between k_{CC}, k_{CT}, and k_{TC}.

The main result of the present kinetic analysis of the 2-butene cyclodimerization is the excellent agreement between the observed distribution of the four isomers of the cyclodimer and the computed curves based on the reaction scheme considered above. This agreement shows that the course of cyclodimerization can be explained quantitatively in terms of the proposed simple mechanism.

Effect of Dilution. The very drastic effect of dilution with isopentane in suppressing photochemical cyclodimerization of *cis*-2-butene (Table IV) can be discussed in terms of the following extension of the earlier reaction scheme.

$$\text{Cis} + h\nu \rightarrow \text{Cis*} \qquad (\text{Iac})$$

$$\text{Cis*} + \text{Cis} \rightarrow \alpha\text{A} + (1 - \alpha)\text{B} \qquad (k_{CC})$$

$$\text{Cis*} + \text{Cis} \rightarrow \gamma\text{Tr} + \delta\text{B}_1 + (2 - \gamma - \delta)\text{Cis} \qquad (k_{Ci})$$

$$\text{Cis*} + \text{Cis} \rightarrow \text{fragmentation} \qquad (k_{Cf})$$

$$\text{Cis*} + \text{IP} \rightarrow \gamma'\text{Tr} + \delta'\text{B}_1 + (1 - \gamma' - \delta')\text{Cis} + \text{IP} \qquad (k'_{Ci})$$

$$\text{Cis*} + \text{IP} \rightarrow \text{fragmentation} \qquad (k'_{Cf})$$

B_1 stands for 1-butene (plus any methylcyclopropane) and IP for isopentane.

Assuming, as before, steady-state concentration for Cis*, it is found that

$$\frac{r_{Tr}}{r_{A+B}} = \frac{\gamma k_{Ci}}{k_{CC}}\left\{1 + \frac{\gamma'}{\gamma}\frac{k'_{Ci}}{k_{Ci}}\frac{[\text{IP}]}{[\text{Cis}]}\right\} \qquad (7)$$

The data in Table IV are in agreement with eq 7, as shown in Figure 2. However, the scatter of the points is appreciable, and, moreover, at greater dilutions fairly large conversions had to be used. The slope to intercept ratio gives a value of about 2.5 for $\gamma' k'_{\mathrm{Ci}}/\gamma k_{\mathrm{Ci}}$. The value larger than unity suggests that cyclodimerization occurs perhaps only within a restricted range of mutual orientations of the two 2-butene molecules at the time of their encounter.

It should be stressed that although the reaction scheme employed treats formally the effect of dilution as a competitive collisional deactivation, implicit in the treatment is the notion that the diluent decreases the probability of encounters (or perhaps of complex formation as a precursor to cyclodimerization) between a ground state and an electronically excited state of *cis*-2-butene during the effective lifetime of the latter. This effect could be to some extent likened to a solvent cage effect.

The ratios of the yields of the other butene isomerization products (butene-1 + methylcyclopropane, not shown in Table IV) to the yield of *trans*-2-butene are not affected by dilution. The effect of dilution on the acyclic C_8 products in Table IV will be discussed in the next section.

Fragmentation Reactions and Cyclodimer Rearrangement. The data in Tables II, III, and IV show that, even in the liquid phase, an appreciable fragmentation (photolysis) of 2-butene takes place and is followed by the usual free radical combination and disproportionation reactions. The extent of photolysis is greater at room temperature than at −78 °C and is much enhanced by a decrease in wavelength to 184.9 nm, at which wavelength relatively little cyclodimerization is observed. These trends are easily understandable in terms of the large amount of energy acquired by the molecule which absorbs a photon (and perhaps enhanced formation of a different electronic state at 184.9 nm[11,12]) and the greater probability of dissipation of energy in liquid phase. In agreement with this, Table III shows very much enhanced photolysis in the gas phase relative to geometric isomerization and very little cyclodimerization even at 213.9 nm. It is not the primary object of the present paper to discuss in detail the mechanism of photolysis, although, as already stated, most of the reaction paths leading to the products listed in Tables II, III, and IV are obvious (and have been indicated by writing each compound symbolically as a dimer of the two radicals from which it has been formed by combination).

It should be mentioned also that, at higher temperatures and shorter wavelengths, the photolytic reactions may be accompanied to some extent by partial rearrangement of the "hot" cyclodimer to acyclic C_8 products. This may in particular apply to 3,4-dimethyl-2-hexene (indicated in the tables by the symbol V·sB), which is affected by dilution in a manner which parallels more closely the trend shown by the cyclodimers A and B than by *trans*-2-butene. Support for this view comes also from the fact that some other products which would be expected if free vinylic radical $CH_3\dot{C}{=}CHCH_3$ were present are not observed. The rearrangement may be visualized as ring opening to form a 1,4-biradical, which then rearranges by a 1,5-H atom shift. 3,4-Dimethyl-1-hexene (M_1·sB) may also be formed to a certain extent by cyclodimer rearrangement, although it must also be formed in this system by radical recombination.

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Kinetic Study of Triplet Excimer Formation in Fluid Solution by Means of Phosphorimetry

Takeshi Takemura,* Masayuki Aikawa, Hiroaki Baba, and Yoshio Shindo

Contribution from the Division of Chemistry, Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan.

Received May 14, 1975

Abstract: The kinetics of the triplet excimer formation has been studied by means of phosphorimetry for naphthalene and 1-chloronaphthalene in isooctane at 293 K. The decay of the monomer phosphorescence and the rise and decay of the excimer phosphorescence following flash excitation were observed. From an analysis of the results obtained, the existence of the triplet excimer was confirmed for both naphthalene and 1-chloronaphthalene. The time behavior of the monomer and excimer phosphorescence is well explained by eq 6 in the text. In isooctane at 293 K the rate constants for the various processes involved were found to be: $k_1 = 0.2 \times 10^3\ \mathrm{s^{-1}}$, $k_2 = 0.8 \times 10^3\ \mathrm{s^{-1}}$, $k_{\mathrm{d}} + k_1{}' = 2.0 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}$, and $k_{\mathrm{dis}} = 7.0 \times 10^3\ \mathrm{s^{-1}}$ for naphthalene, and $k_1 = 0.6 \times 10^3\ \mathrm{s^{-1}}$, $k_2 = 0.6 \times 10^3\ \mathrm{s^{-1}}$, $k_{\mathrm{d}} + k_1{}' = 6.0 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}$, and $k_{\mathrm{dis}} = 1.0 \times 10^3\ \mathrm{s^{-1}}$ for 1-chloronaphthalene.

The excimer phosphorescence or the triplet excimer has been studied by several workers for aromatic compounds under various conditions.[1-14] Existence of the triplet excimer is relatively well established for some halobenzenes.[3,4] Langelaar et al.[6] indirectly obtained excimer phosphorescence spectra for naphthalene and phenanthrene by subtracting the phosphorescence spectrum at 140 K (just below the melting point of the solvent, 95% ethanol) from the spectrum at higher temperatures, but the emission assigned to the triplet excimer of phenanthrene turned out to origi-

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