A mixture of 250 ml. of aqueous 50% sulfuric acid solution and 80 g. (0.373 mole) of the diether was heated in an oil-bath for 12 hours at 100°. At the end of this time all the diether which was initially in the upper layer had been hydrolyzed and the flask was filled with white solid. Extensive etching occurred due to the reaction of hydrogen fluoride with glass. The solid was filtered and dissolved in 800 ml. of boiling water. Upon cooling the first fraction, 31 g. of diketocyclobutenediol crystallized. A total of 40 g. (0.35 mole) of white diketocyclobutenediol was obtained. It was dried by acetone–ether rinses and placed in an evacuated phosphorus pentoxide desiccator. The 40 g. represent a 94% yield based on the diether. The neutralization equivalent was 57.8; calcd. for the dibasic acid is 57.1. The infrared spectra of the solid acid and potassium salt were identical with that previously prepared from the hydrolysis of the triether. The cyclobutadienoquinone acid appeared to be stable up to 294° at which point it decomposed but did not melt. The diketocyclobutenediol showed the same chemical tests as the previously prepared material; a positive enol test with ferric chloride, oxidation by cerate, permanganate, periodic acid, and bromine water solutions. The dipotassium salt crystallized with one molecule of water of hydration.

Anal. Calcd. for $K_2C_4O_4 \cdot H_2O$; C, 23.07; H, 0.96; H_2O, 8.64. Found: C, 23.32; H, 0.99; H_2O, 8.53.

Quantitative Oxidation with Cerate Solution.—$H_2C_4O_4 + 10\ Ce^{+4} + 4\ H_2O \rightarrow 4CO_2 + 10\ Ce^{+3} + 10H^+$.

A 0.118 *N* ceric sulfate solution was made from hexanitratoammonium cerate according to the procedure of G. Frederick Smith. Ten ml. of an aqueous 0.114 molar solution of diketocyclobutenediol was titrated with the standard cerate solution using the Beckman Zeromatic meter with a platinum indicating electrode and a calomel reference. The curve showed a very steep rise in potential at the equivalence point; 0.55 volt within 2 drops of cerate. The volume of cerate required was 95.2 ml.; *i.e.*, 1.14 ml. of compound required 11.2 meq. of cerate. This, therefore, showed the equivalent weight of the diketocyclobutenediol in oxidation to be 11.4 g. or 1/10 the molecular weight.

The inorganic reactions of the acid are quite interesting as colored precipitates are formed with many metal ions and relatively weak oxidizing agents like ferricyanide are reduced.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH]

Thermal Decomposition of 1,1'-Azobutane, 1,1'-Azoisobutane, 2,2'-Azobutane and 2,2'-Azoisobutane[1-3]

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Four azobutanes have been prepared, each above 99 mole % in purity: 1,1'-azobutane, 1,1'-azoisobutane and 2,2'-azobutane from the appropriate aldehyde or ketone *via* the azine and dialkylhydrazine, and 2,2'-azoisobutane from N-bromo-*t*-butylamine and silver oxide. A flow system, designed so that during the sampling period the reaction products flow directly into a gas chromatographic column, was used to measure the rates of thermal decomposition in a small borosilicate glass reactor tube. Helium and hydrogen were used as carrier gases. Concentrations of approximately 1 and 5% of azo compound in the carrier gas were used. The rate of decomposition was determined by measurement of the nitrogen produced. The decomposition reaction of these azobutanes is first order. The activation energies for R—N=N—R in helium in which R, respectively, is *n*-butyl, isobutyl, *sec*-butyl and *t*-butyl are 53.2, 49.0, 48.4 and 43.0 kcal./mole. For each of the first three, the activation energy determined in hydrogen is less than that in helium. For 2,2'-azoisobutane the values are the same. The gaseous products of the thermal decomposition have been determined for each azobutane in both hydrogen and helium. These data indicate the relative extent of the coupling, disproportionation and decomposition reactions of the four butyl radicals.

Introduction

Free alkyl radicals are transitory species in the thermal decomposition of azoalkanes. In the initial step a molecule of azoalkane decomposes to a molecule of nitrogen and two alkyl radicals.[4-6]

This study was made to provide information concerning azobutanes as sources of four isomeric butyl radicals in the temperature range 200–400°. The kinetics of decomposition of four symmetrical azobutanes have been determined and the gaseous products of decomposition have been analyzed.

Experimental

2,2'-Azobutane.—Methylethyl ketazine was prepared in two ways: (1) by mixing 95% hydrazine and cold ethanol at 0°, then slowly adding freshly distilled butanone, and refluxing for 6 hours[7]; and (2) by slowly adding hydrazine hydrate to twice the number of moles of butanone in diethyl ether at 0°, stirring at room temperature for 2 hours, distilling the ether, and drying with anhydrous potassium carbonate.[8] Better yields were obtained by the second method. The methylethyl ketazine was hydrogenated[9-12] in an equivalent of glacial acetic acid dissolved in ethanol with platinum oxide and hydrogen at 60 p.s.i.g. The hydrogenation was complete in 5 to 7 days. The reaction mixture was filtered to remove platinum and made basic with 10 *M* sodium hydroxide. The ethanol was removed by extraction with water. The product was dried with potassium carbonate. Vacuum fractionation through a 25-inch Vigreux column gave 1,2-di-*sec*-butylhydrazine (b.p. 73–78° (25 mm.), 75% average yield).

This compound was oxidized by direct addition of an equivalent of mercuric oxide[11,12] in small portions. The mixture was heated on a steam-bath for 1 hour and then let

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(2) Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 7, 1961.

(3) Abstracted in part from a thesis submitted by Norman L. Eatough in partial fulfillment of the requirements for the degree of Master of Science, Brigham Young University.

(4) F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.*, **55**, 3898 (1933).

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(10) A. Skita and W. Meyer, *Ber.*, **45**, 3579 (1912) [*C.A.*, **7**, 2557 (1913)].

(11) K. A. Taipale, *J. Russ. Phys. Chem. Soc.*, **56**, 81 (1925) [*C.A.*, **19**, 3478 (1925)].

(12) K. A. Taipale, *ibid.*, **57**, 487 (1925) [*C.A.*, **20**, 3282 (1926)].

TABLE I

PHYSICAL PROPERTIES OF AZO COMPOUNDS, DIALKYLHYDRAZINES AND AZINES

R	B.p., °C. (mm.)		Density		Refractive index		Lit. ref.
	Obsd.	Lit.	Obsd. d^{25}_4	Lit. d_4 (°C.)	Obsd. n^{20}_D	Lit. n_D (°C.)	
Azo compounds, R—N=N—R							
n-Butyl	69–70 (28)		0.7828		1.4179		
s-Butyl	50–51 (27)	141–142 (747)	.7705	0.7689 (25)	1.4093	1.4064 (25)	14
Isobutyl	55–56 (29)	145 (752)	.7702		1.4110		11
t-Butyl	48.0 (80)	109–110 (760)	.7441	.7670 (20)	1.3961	1.4091 (20)	13
		107–108				1.3940 (25)	15
		108–109		.7617 (20)			16
Dialkylhydrazines, R—HN—NH—R							
n-Butyl	83–84 (12)		0.8124		1.4380		
s-Butyl	77 (25)	168–170 (750)	.8036	0.8005 (25)	1.4300	1.4246 (25)	14
Isobutyl	72 (16)	70.5 (16)	.8001		1.4312		11
Azines, R=N—N=R							
n-Butylidene	72 (12)	80 (26)	0.8163	0.8315 (20)	1.4512	1.4520 (20)	17
s-Butylidene	76–77 (22)	85.7 (37)	.8359	.8404 (20)	1.4542	1.4516 (26.6)	18
		168–170 (750)		.8341 (25)		1.4513 (25)	14
Isobutylidene	63 (17)	88 (79)	.8117	.8247 (26)	1.4447	1.4472 (20)	17
		63 (14)					19
		160–165					7

stand for 1 or 2 days at room temperature. The liquid product was decanted and dried with potassium carbonate. Approximately 25% of the mercuric oxide remained unreacted. Fractional distillation gave 2,2'-azobutane (b.p. 49–52° (27 mm.), 45%) and a higher boiling fraction which was not investigated further (b.p. 55–82° (27 mm.)).

1,1'-Azoisobutane.—Isobutyraldehyde and hydrazine reacted to give isobutyraldazine by both methods described above, the second method giving a better yield (b.p. 65–69° (20 mm.), 68%). Hydrogenation to give 1,2-diisobutylhydrazine (b.p. 70–76° (20 mm.), 64%) occurred at a more rapid rate than the hydrogenation of methylethyl ketazine. Oxidation with mercuric oxide to give 1,1'-azoisobutane (b.p. 50–53° (24 mm.), 68%) was more vigorous than that of 1,2-di-*sec*-butylhydrazine with approximately 15% of the mercuric oxide remaining unreacted.

1,1'-Azobutane.—*n*-Butyraldehyde and hydrazine reacted more vigorously as compared with the other azine preparations. For a representative preparation by procedure 1 the distillation of the reaction mixture gave two fractions (I, b.p. 74–86° (21 mm.), 35%; II, b.p. 86–92° (21 mm.), 35%). A gradual temperature rise was observed. White crystals precipitated from fraction I after 1 hour. This material was not investigated further. Only fraction II was used for the subsequent hydrogenation. When procedure 2 was used the yield of the azine improved (b.p. 81–86° (20 mm.), 60%) and the yield of the white crystalline material was considerably reduced. Hydrogenation as described above gave 60% yield of 1,2-di-*n*-butylhydrazine (b.p. 80–85° (12 mm.)). In subsequent runs it was observed that when the ratio of solvent to *n*-butyraldazine was increased to 2:1 the hydrogenation could be effected within 24 hours. Oxidation gave a more vigorous reaction than in either of the two previous oxidations with mercuric oxide. Approximately 30% of the mercuric oxide remained unreacted after 2 days. The average yield of 1,1'-azobutane was 47% (b.p. 62–68° (23 mm.)).

2,2'-Azoisobutane.—The procedure of Farenhorst and Kooyman[13] was scaled up about ten times. From four batches 80 g. of crude 2,2'-azoisobutane was obtained (b.p. 47–50° (80 mm.)).

Purity and Physical Properties.—The azines and dialkylhydrazines were purified by distillation through a 25-inch Vigreux column at reduced pressure. The center fraction was used to determine the physical properties reported in Table I. The azo compounds were purified by vacuum fractional distillation through a 40-inch Todd column packed with glass helices. A reflux ratio of 25:1 was maintained. The center, constant boiling fractions were used to determine the physical properties reported in Table I. These fractions were subsequently used in the decomposition studies. Densities were measured with a 10-ml. pycnometer in a water-bath held at 25.00 ± 0.01°. Refractive indices were taken with an Abbe refractometer at 20.0 ± 0.1°. Infrared spectra were taken but will not be included as part of this article.

The purities of the azo compounds were determined by the method of Nelson[20] and are reported in Table II. The samples of azo compounds referred to in Table II were used in the kinetic determinations in which helium was used as the carrier gas. For the kinetic determination with hydrogen as the carrier gas, less pure samples of the first three azobutanes were used; the values of mole % purity are 96.3 ± 0.6, 99.7 ± 0.1, 98.5 ± 0.3, respectively.

TABLE II

MELTING POINTS AND PURITY

Butane	M.p., °C.		Estd. ΔH_{fusion}, kcal.	Purity, mole %
	Obsd.	Corr. to zero impurity[20]		
1,1'-Azo-	−78.3	−78.1	3.5 ± 0.2	99.1 ± 0.2
2,2'-Azo-	−61.9	−61.9	3.1 ± .5	99.9 ± .1
1,1'-Azoiso-	−73.0	−72.9	3.2 ± .6	99.7 ± .1
2,2'-Azoiso-	−12.5	−12.4	1.3 ± .6	99.9 ± .1

A vapor pressure curve for each azo compound was determined by measuring the reflux temperature at each of several pressures in the 25-inch Vigreux column. Since the physical properties of 1,1'-azobutane have not been reported previously, a purified sample was analyzed.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.55; H, 12.76; N, 19.69. Found: C, 67.57; H, 12.80; N, 19.63.

Apparatus.—A diagram of the apparatus used in the thermal decomposition studies is shown in Fig. 1. The carrier gas, either hydrogen or helium from a commercial cylinder, was passed through a 6-inch silica gel column and then split into two streams. Stream I passed, in turn, through a flowmeter, two bubblers containing the azo compound (the first held at a slightly higher temperature[21] than the second).

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[13] E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953).

[14] L. D. Barrick, G. W. Drake and H. L. Lochte, *J. Am. Chem. Soc.*, **58**, 160 (1936).

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[18] T. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 165 (1891).

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[21] K. A. Wilde, *J. Phys. Chem.*, **61**, 385 (1957).

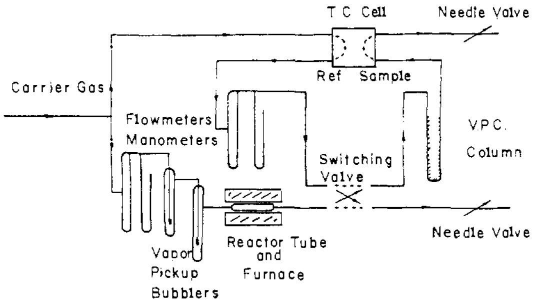

Fig. 1.—Apparatus.

the reactor tube in a Fisher micro-combustion furnace, a switching device to interchange gas streams, and a needle valve opening to the atmosphere. Stream II passed, in turn, through the reference channel of a Gow-Mac thermal conductivity cell model TE-2, a flowmeter, the switching device, the gas chromatographic column, the sampling channel of the thermal conductivity cell, and a needle valve opening to the atmosphere. A manometer was placed by each flowmeter.

During a run, the two gas streams flowed through the systems as indicated above. The pressures and rates of flow of the two streams were controlled by the needle valves. Equal pressures were maintained in the two streams to permit the rates of flow in both streams to remain nearly constant before and during the sampling period. A sample was taken by interchanging streams I and II with the switching device (constructed from two three-way stopcocks). After the sampling period the switch was quickly returned to its original position and the rate of flow of stream II increased to the elution rate.

The dimensions of the Pyrex reactor tube and the temperature profile through the tube are shown in Fig. 2. In computing contact times, the volume of the center part of the tube was used. Two reactor tubes were used having volumes of 2.53 ml. and 5.82 ml.

Temperatures were measured with iron constantan thermocouples connected to a Wheelco portable potentiometer model 310. In actual operation the thermocouple was placed between the reactor tube and a surrounding tube. The necessary corrections to give the temperature inside the tube were determined.

The first bubbler was constructed with a vapor reflux jacket and maintained at a temperature 3–4° higher than the second; the second was immersed in a water-bath controlled to ±0.05° of the desired temperature with a Lapine Tempunit.

Preliminary studies indicated that there was some entrainment of small droplets of azo compound as the carrier gas passed through the bubblers, the second bubbler was packed with a 4-inch column of Pyrex glass wool to remove these droplets from the gas stream. When the temperature of the bubblers was above room temperature it was necessary to heat the tubing from the bubblers to the reactor with coiled nichrome wire and an Electrothermal heating tape to prevent condensation of the azo compound.

The effectiveness of the bubblers was determined by comparing the amount of 2,2′-azobutane deposited on a short chromatographic column at −70° with the amount calculated from the vapor pressure of the azo compound. Excellent agreement was observed.

The rate of decomposition was followed by measuring the amount of nitrogen evolved; the amount of nitrogen was determined with a 24-inch gas chromatographic column of 45/65 mesh silica gel held at the temperature of solid CO_2 in a CCl_4–$CHCl_3$ bath.[22] Nitrogen and methane were the only reaction products eluted under these conditions. The nitrogen peak areas were calibrated by injecting known quantities of nitrogen into the system.

The flowmeters were calibrated and a reproducibility of ± 0.1 ml./min. was observed.

Procedure for Determination of Kinetics.—The following data were recorded for each sample

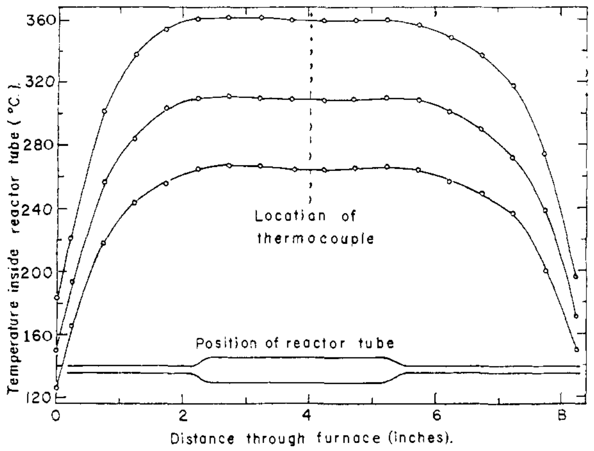

Fig. 2.—Temperature distribution through the reactor tube in the furnace.

f_1 = rate of flow of carrier gas through flowmeter (1) at time of sampling
f_2 = rate of flow of carrier gas at the time of elution
p_1 = press. in stream (1) at flowmeter (1) at time of sampling
p_2 = press. in stream (2) at flowmeter (2) at the time of elution
P_v = vapor press. of the azo cmpd. at temperature of second bubbler
P = atmospheric pressure
T_1 = ambient temperature
T_2 = temperature of the reactor
T_3 = temperature of the second bubbler
v_r = volume of the reactor
A = nitrogen peak area
t_s = time of sampling as indicated by a stopwatch

The decomposition was assumed to be first order as previous studies of azoalkanes have shown.[6,16] Modification of the integrated rate equation, $kt = \ln([Azo]_0/[Azo]_t)$ to conform to the experimental terms above gave

$$kt_c = \ln\frac{n_0}{n_t} = \ln\frac{n_0}{n_0 - n_{N_2}}$$

The ratio of initial to final concentration of azo compound for a single sample ($[Azo]_0/[Azo]_t$) was assumed to be the ratio of the number of moles of azo compound in the sample before and after decomposition (n_0/n_t). This assumption is valid if the volume of the gaseous sample remains the same during the decomposition. Even though a molecule of an azobutane may decompose to two or more product molecules, the carrier gas is 95% or 99% of the initial gas stream and the error in representative values of $\ln([Azo]_0/[Azo]_t)$ due to increase in volume during decomposition was estimated to be < 1%.

The elapsed time of reaction (t) was taken as the calculated contact time (t_c)

$$t_c = \frac{\text{volume of reactor}}{\text{rate of flow of gases at } T_2} = \frac{v_r T_1}{T_2\left(\dfrac{f_1}{1 - (P_v/(P + p_1))}\right)}$$

The number of moles of azo compound (n_0) originally in a sample was calculated from the equation

$$n_0 = \frac{P_v f_1 t_s}{R\,T_1\left(1 - \dfrac{P_v}{P + p_1}\right)}$$

The number of moles of azo compound decomposed is equal to the number of moles of nitrogen (n_{N_2}) released. This quantity was determined from the nitrogen peak area (A).

For each compound at constant concentration in a particular carrier gas, specific rate constants (k) at from four to seven temperatures were plotted according to the equation $k = Ae^{-(E_a/RT)}$ to determine the energy of activation (E_a) and the frequency factor (A). The entropy of activa-

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[22] D. H. Szulczewski and T. Higuchi, *Anal. Chem.*, **29**, 1541 (1957).

TABLE III

DECOMPOSITION OF AZOBUTANES. SUMMARY OF SPECIFIC RATE CONSTANTS

Concn., mole % in carrier	T, °C.	k, sec.$^{-1}$	Concn., mole % in carrier	T, °C.	k, sec.$^{-1}$
		1,1′-Azobutane			
1.1% in helium	380	0.950	4.6% in helium	367	0.400
	364	.230		357	.200
	345	.780		336	.0444
	323	.0175		319	.0115
				305	.0044
0.7% in hydrogen	382	0.753	2.9% in hydrogen	363	0.323
	367	.387		355	.212
	357	.213		344	.102
	342	.096		334	.052
	333	.0565		318	.020
				310	.0107
		2,2′-Azobutane			
1.2% in helium	345	1.42	4.1% in helium	315	0.173
	322	0.348		294	.035
	304	.091		274	.0084
	282	.018		257	.0014
	266	.0045			
1.5% in hydrogen	355	2.04	6.3% in hydrogen	321	0.240
	341	0.842		309	.131
	330	.515		292	.044
	308	.127		281	.020
	289	.033			
	273	.0086			
		1,1′-Azoisobutane			
1.1% in helium	379	0.595	4.8% in helium	379	0.644
	362	.215		366	.306
	341	.058		352	.117
	325	.0225		327	.0234
	315	.0083		315	.0104
				293	.0021
1.2% in hydrogen	381	0.597	5.4% in hydrogen	365	0.370
	378	.493		361	.293
	363	.241		351	.164
	355	.173		342	.072
	346	.091		331	.038
	334	.053		320	.019
	319	.020		315	.014
				307	.0082
		2,2′-Azoisobutane			
0.9% in helium	286	2.29	4.3% in helium	275	1.08
	273	0.96		257	0.296
	261	.267		238	.052
	241	.060		211	.0058
	220	.013		199	.0018
0.97% in hydrogen	291	2.21	4.6% in hydrogen	266	0.517
	272	0.77		243	.083
	247	.131		224	.0164
	222	.0098		206	.0031

tion was calculated[23] from A by the equation

$$\Delta S^* = R \ln (Ah/kTe)$$

Analysis of Gaseous Products of Decomposition.—The gaseous products of decomposition were determined by gas chromatographic analysis. Two columns were used in series: (1) a 3-foot column of dioctyl phthalate on firebrick; and (2) a 9-inch column of silica gel. These columns were connected directly in the system to avoid transferring the sample. The columns were short so that an adequate rate of flow could be maintained during sampling. The separation was made by holding column 1 at 0° and column 2 at −80° while the sample was taken. The C_4-hydrocarbons remained in column 1, C_2- and C_3-hydrocarbons remained in column 2 and nitrogen and methane were eluted. Column 1 was by-passed and column 2 raised to 15° to separate and elute ethane and ethylene. Column 2 was then raised to 65° to separate and elute propane and propylene. Column 2 was then by-passed and column 1 eluted. The C_4-fraction gave three peaks: first, isobutane; second, n-butane, 1-butene and isobutylene; third, 2-butene. The ratio of components in the second peak was determined by condensing a sample and analyzing it on a Fisher–Gulf partitioner. This procedure was standardized against actual samples of these gases.

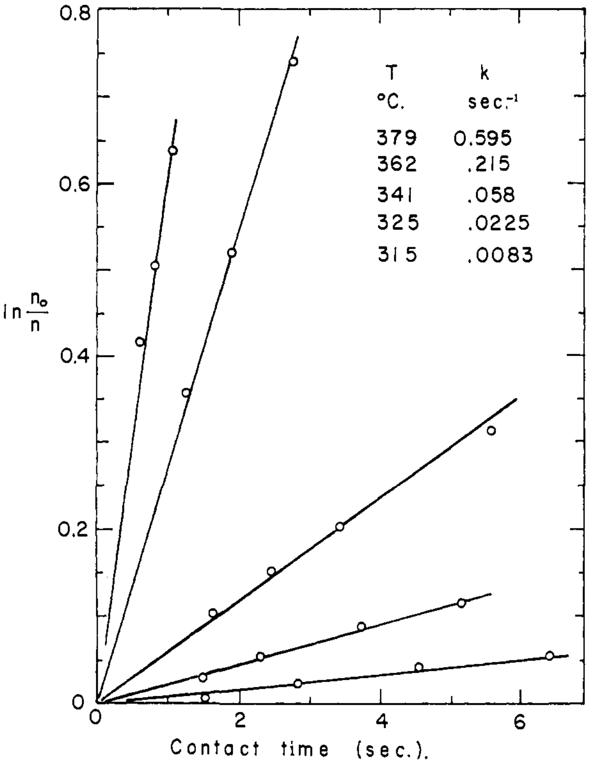

Fig. 3.—Decomposition of 1,1′-azoisobutane (1.1% vapor in helium).

Results

For each of the four azobutanes, rate studies were made at two concentrations of the azo compound in both helium and hydrogen as carrier gases. From these data, sixteen graphs of ln (n_0/n_t) *vs.* t_c were constructed. One of these is given in Fig. 3. Each experimental point is an average of two or three determinations. From these graphs specific rate constants were determined, a summary of which is given in Table III.

From the rate data of Table III graphs of ln k *vs.* T^{-1} were constructed by visually fitting a straight line to each set of data points. In this way the activation energy, E_a, and frequency factor, A, were determined for each set of data.

Later these same data were processed with an IBM 650 computer using a least squares program for determining E_a, A, and the entropy of activation, ΔS^* (calculated at 300°). For each set of data the value of E_a by the least squares method was different from the value of E_a determined visually. This difference in E_a varied from 0.1 to 2.0 kcal./mole through the sixteen sets of data.

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[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 96-100.

For each azobutane the values of E_a as a function of concentration of azobutane in helium were the same, within the error limits. However, for two of the azobutanes the values of E_a were lower for the smaller concentration of azobutane in hydrogen than for the higher concentration. Where the values of E_a were essentially the same for a particular azobutane, the two sets of rate data were combined and reprocessed with the least squares program. These values are reported in Table IV. The error limits assigned to E_a reflect the differences described above. Although not indicated, comparable error limits are to be considered in the values of A and ΔS^*.

TABLE IV

THERMAL DECOMPOSITION OF AZOBUTANES

Compound	E_a, kcal./mole	A, sec.$^{-1}$	ΔS^* (300°), e.u.
	Helium as carrier gas		
1,1'-Azobutane	53.2 ± 0.6	5.1×10^{15}	19
1,1'-Azoisobutane	$49.0 \pm .5$	1.7×10^{16}	12
2,2'-Azobutane	$48.4 \pm .6$	1.9×10^{17}	17
2,2'-Azoisobutane	$43.0 \pm .5$	1.4×10^{17}	17
	Hydrogen as carrier gas		
1,1'-Azobutane (0.7%)	42.0 ± 1.0	8.3×10^{13}	2
(2.9%)	47.3 ± 1.0	5.8×10^{15}	10
1,1'-Azoisobutane (1.2%)	41.6 ± 0.6	4.9×10^{13}	1
(5.4%)	48.8 ± 1.5	1.9×10^{16}	13
2,2'-Azobutane	43.0 ± 1.8	1.7×10^{15}	8
2,2'-Azoisobutane	43.0 ± 0.8	1.3×10^{17}	16

For each azobutane the composition of the gaseous products of decomposition (nitrogen and C_1- to C_4-hydrocarbons) was determined at two temperatures and two concentrations of both helium and hydrogen as carrier gases. These data were converted to mole per cent. and are presented in Table V. The error limits of these values were not determined.

Discussion

The results support the first-order decomposition of these azobutanes in helium as the carrier gas. They decompose at rates which are suitable for their use as sources of free radicals in the temperature range 200–400°. For any particular temperature in this range 2,2'-azoisobutane decomposes most rapidly and 1,1'-azobutane most slowly. This relationship is shown more quantitatively by comparing the calculated half-lives of these azobutanes at 300°: 0.13, 11, 200, 250 seconds, respectively, for the *t*-butyl, *sec*-butyl, isobutyl and *n*-butyl compounds.

The activation energies (43.0 kcal.) reported here for the decomposition of 2,2'-azoisobutane in a flow system with both helium and hydrogen as carrier gases are in satisfactory agreement with the value (42.8 kcal.) reported by Levy and Copeland[16] for decomposition in a static system.

The activation energies for the series of isomeric azobutanes appear to be a function of the structure of R in R—N=N—R: E_a(primary) > E_a(secondary) > E_a(tertiary).

With hydrogen as the carrier gas, satisfactory first-order graphs were obtained also. However, at least four observations indicate that some kind of interaction of three of the azobutanes with hydrogen occurs during the decomposition: (1) the lower activation energies for three of the azobutanes in hydrogen as compared with helium; (2) the change in activation energies for 1,1'-azobutane and 1,1'-azoisobutane as a function of the concentration of the azo compound in hydrogen; (3) the lower entropies of activation for three of the azobutanes in hydrogen as compared with helium; (4) the greater ratio of saturated to unsaturated gaseous decomposition products in hydrogen as compared with helium.

These observations suggest a more ordered or tightly bound transition state for the decompositions in hydrogen than those in helium. Less energy is required to transform the bonds to the activated complex. It is possible that hydrogen enters directly into the formation of the activated complex giving a more ordered system with resultant lowering of the entropy of activation. The decomposition in hydrogen may be a two-step process, the slower step being first order and making the over-all decomposition appear first order. Such a decomposition would have an equal or lower energy of activation as compared with a one-step decomposition in helium.

Products of Decomposition.—Although only the gaseous products of decomposition (nitrogen and C_1- to C_4-hydrocarbons) were analyzed, certain inferences can be made concerning the other products of decomposition. Our interpretation of the decomposition of each azobutane in helium is based on the relative molar amount of nitrogen in the gaseous products. The percentage value of nitrogen when considered as a molar quantity indicates that twice that number of moles of butyl radicals are released. The various reactions of butyl radical are indicated by the corresponding molar amounts of the gaseous products. The portion of butyl radicals not accounted for is assumed to have reacted by dimerization or coupling to form C_5- to C_8-hydrocarbons.

Moore and Wall[24] have observed the decomposition of *n*-butyl to ethyl and ethylene, and *sec*-butyl or isobutyl to methyl and propylene. Similarly, for three of the azobutanes, decomposition of the respective butyl radicals is the major or one of the major reactions.

2,2'-Azoisobutane.—The mole percentage composition of the gaseous products from the decomposition of about 1% 2,2'-azoisobutane in helium at 290° is: nitrogen, 46%; isobutane, 26%; and isobutylene, 28%. Our interpretation of these data is that as 46 moles of the azobutane decompose, 92 moles of *t*-butyl radicals are released, of which 54 moles react by disproportionation to give 27 moles each of isobutane and isobutylene (which is approximately what our analysis shows). The remaining 38 moles of *t*-butyl radicals are assumed to react by dimerization to a branched octane. Levy and Copeland[16] found tetramethylbutane in their study of the decomposition of 2,2'-azoisobutane.

From this interpretation which is summarized in Table VI the percentages of *t*-butyl radicals reacting by disproportionation and dimerization

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[24] W. J. Moore and L. A. Wall, *J. Chem. Phys.*, **17**, 1325 (1949).

TABLE V

GASEOUS PRODUCTS OF DECOMPOSITION

Concn. of azobutane, mole % in carrier	T, °C.	Composition of gaseous products, mole % Nitrogen	Methane	Ethane	Ethylene	Propane	Propylene	Isobutane	Isobutylene	n-Butane	1-Butene	2-Butene
					1,1'-Azobutane							
0.9% in He	446	28.3	0.2	3.9	45.8	3.9				17.8		
	392	26.5	.1	4.3	48.7	1.6				18.9		
4.6% in He	467	29.1	.1	4.9	46.5	1.1				18.2		
	396	29.1	.1	6.0	46.3	1.7	0.2			16.7		
0.9% in He$_2$	463	20.8	3.1	37.0	27.7	2.9	1.5			7.0		
	417	23.5	5.3	38.8	21.7	3.3	0.9			6.6		
4.6% in H$_2$	459	24.8	2.2	20.6	36.3	1.7	1.8			9.0		
	407	25.5	2.1	25.3	33.6	1.8	1.5			10.0		
					2,2'-Azobutane							
1.5% in He	381	39.0	0.7	7.4			39.8			7.4	3.2	2.5
	345	48.2	0.6	4.1			30.3			8.1	3.8	4.1
6.3% in He	377	47.5	2.2	4.3			24.2			9.6	4.4	7.5
	340	53.0	1.7	1.7			18.1			12.6	6.0	6.6
1.5% in H$_2$	368	42.6	20.0	5.0		2.3	11.8			15.1	1.3	1.2
	335	42.8	10.8	2.8		3.4	12.3			21.7	1.9	3.2
4.9% in H$_2$	368	42.0	10.3	3.6		3.0	19.4			16.6	1.4	3.2
	335	47.3	7.6	1.8		1.2	11.7			21.6	2.0	5.6
					1,1'-Azoisobutane							
1.2% in He	445	29.1	7.3	16.3		0.7	41.8	2.8	2.1			
	383	32.2	9.7	13.3		1.6	37.1	3.2	2.8			
6.0% in He	438	33.9	7.6	12.5		1.3	38.2	3.2	3.3			
	386	30.4	9.8	9.3		1.5	40.6	4.5	3.8			
1.2% in H$_2$	434	27.0	23.0	4.8		16.1	20.5	7.3	1.2			
5.0% in H$_2$	434	25.6	15.8	5.3		7.8	28.9	12.1	3.2			
	379	30.9	15.0	2.7		7.1	29.0	12.2	2.9			
					2,2'-Azoisobutane							
0.9% in He	290	45.5						26.2	28.3			
	261	48.6						23.3	28.1			
4.1% in He	290	43.7						27.4	28.8			
	247	38.9						31.0	30.1			
0.95% in H$_2$	293	53.2						25.6	21.3			
	252	48.9						28.5	22.7			
4.5% in H$_2$	291	46.4						27.6	26.0			
	250	56.5						18.1	25.4			

TABLE VI

DECOMPOSITION OF 2,2'-AZOISOBUTANE

Conditions, 0.9% in helium at 290°

Gaseous products mole %		Interpretation	
N$_2$	46	t-Butyl released	92 moles
i-C$_4$H$_{10}$	26	Disproportionation	54
i-C$_4$H$_3$	28	Dimerization	38

Reactions

$$t\text{-Butyl}\ \begin{array}{l} \nearrow\ \text{Isobutylene} + \text{isobutane} \\ \searrow\ \text{Branched octane} \end{array}$$

Comparison

Concn.	Temp., °C.	% t-Butyl reacting by Dispr.	Dimer.
0.9% in He	290	59	41
	261	52	48
4.1% in He	290	64	36
	247	78	22

are determined. These values are compared with values obtained in a similar way but for other conditions of temperature and concentration. This suggests that the ratio of the rate constants of the disproportionation and dimerization reactions is 1.4; similarly at 247° with about 4% 2,2'-azoisobutane in helium the ratio calculated is 3.6. These values, when compared with the value 4.59 which Kraus and Calvert[25] report, seem too low especially at the higher temperature. The assumption that the only condensed product is the dimer, tetramethylbutane, may be in error. Further discussion of this difficulty will be deferred pending analysis of the condensed phase from the decomposition.

Levy and Copeland[16] found no isobutylene in their determinations, suggesting that the isobutylene from the disproportionation reacts with t-butyl radicals to give isobutane and methallyl radicals. The methallyl radicals then dimerize and react further to give a brown deposit on the surface of the reaction vessel. However our results show that about equal amounts of isobutylene and isobutane are recovered from the decomposition. Apparently the secondary reactions that occur in the static system[16] are prevented from occurring

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[25] J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

in the flow system by rapid removal of the primary decomposition products. Also, there may be a reduction in reactivity of the *t*-butyl radicals for hydrogen abstraction of isobutylene. That is, the *t*-butyl radicals, before reaction, may approach thermal equilibrium by collision with helium atoms.

2,2′-Azobutane.—The mole percentage composition of gaseous products from the decomposition of about 1.5% 2,2′-azobutane in helium at 381° is: nitrogen, 39%; propylene, 40%; *n*-butane, 7%; ethane, 7%; 1-butene, 3%; 2-butene, 3% and methane, 1%. Neither ethylene nor propane was detected. Our interpretation of these data is that as 39 moles of 2,2′-azobutane decompose, 78 moles of *sec*-butyl radicals are released, of which 13 moles disproportionate to *n*-butane and the butenes, 41 moles decompose to propylene and methyl radicals and 24 moles either dimerize or couple with methyl radicals. Of the 41 moles of methyl radicals, 14 moles dimerize to give 7 moles of ethane, 1 mole abstracts hydrogen from propylene to give 1 mole of methane and 1 mole of allyl radicals which dimerize or couple with other radicals to form higher molecular weight condensation products. Sehon and Szwarc[26] have shown that allyl radicals are sufficiently stable to do this.

This leaves 26 moles of methyl radicals, part of which couples with *sec*-butyl and part possibly adds to the unreacted azo compound.

From this interpretation, which is summarized in Table VII, the percentages of *sec*-butyl radicals reacting by disproportionation, decomposition and coupling are determined. These values are compared with values obtained in a similar way but for other conditions of temperature and concentration.

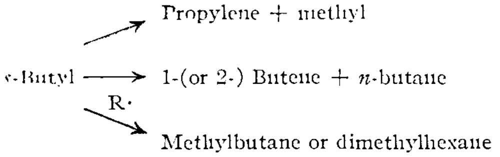
TABLE VII

DECOMPOSITION OF 2,2′-AZOBUTANE

Conditions, 1.5% in helium at 381°

Gaseous products	mole %	Interpretation	
N_2	39	*s*-Butyl released	78 moles
CH_4	1	Disproportionation	13
C_2H_6	7	Decomposition	41
C_2H_4	0	Coupling	24
C_3H_8	0		
C_3H_6	40	Methyl released	41 moles
n-C_4H_{10}	7	Dimerization	14
1-C_4H_8	3	H-abstraction	1
2-C_4H_8	3	Coupling or addition	26

Reactions



Comparison

Concn.	Temp., °C.	% *s*-butyl reacting by— Decom.	Dispr.	Coupl.
1.5% in He	381	52	17	31
	345	32	17	51
6.3% in He	377	27	23	50
	340	19	24	57

A significant feature here is that the extent of radical decomposition is increased with a rise in temperature and with a decrease in the concentration of the azo compound.

Two coupling reactions are suggested: (1) dimerization of *sec*-butyl radicals and (2) coupling of *sec*-butyl radicals with methyl radicals. On the basis of the value 2.27 for $k_{\text{disproportionation}}/k_{\text{combination}}$ of Kraus and Calvert,[24] about 4 to 6 times the number of *sec*-butyl radicals react by coupling with methyl radicals as dimerize under the conditions of temperature and concentration in this study.

1,1′-Azobutane.—In a similar way, our interpretation of the composition of gaseous product from a representative decomposition of 1,1′-azobutane in helium is given in Table VIII.

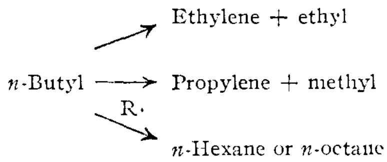
TABLE VIII

DECOMPOSITION OF 1,1′-AZOBUTANE

Conditions, 0.9% in helium at 446°

Gaseous products	mole %	Interpretation		
N_2	28	*n*-Butyl released		56 moles
CH_4	0.2	Disproportionation		0
C_2H_6	4	Decomposition to	Et	46
			Me	4
C_2H_4	46	Coupling		6
C_3H_8	4	Ethyl released		46 moles
C_3H_6	0	Dimerization		36
n-C_4H_{10}	18	H-abstraction		4
1-C_4H_8	0	Coupling	with Me	4
			with Bu	2
2-C_4H_8	0	Methyl released		4 moles
		Coupling with Et		4

Reactions of *n*-butyl



Comparison

Concn.	Temp., °C.	% *n*-Butyl reacting by— Decomposition to Et	to Me	Coupling
0.9% in He	446	82	8	11
	392	90	4	6
4.6% in He	467	81	2	17
	396	79	4	17

The rather striking features here are the large quantity of ethylene and the absence of butenes even though butane is present. With the absence of 1-butene and 2-butene no apparent disproportionation of the *n*-butyl radicals has occurred. The large amount of ethylene is explained by decomposition of *n*-butyl radicals to ethylene and ethyl radicals. Most of the ethyl radicals dimerize to *n*-butane.

The presence of propane and the absence of propylene are explained by the assumption of an alternative path for decomposition of *n*-butyl radicals in which propylene and methyl radicals are produced.[27] In the presence of a relatively

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(26) A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A202**, 263 (1950).

(27) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press Inc., New York, N. Y., 1955, p. 303.

high concentration of ethyl radicals, the methyl radicals couple with ethyl radicals to give propane; and the ethyl radicals abstract the allylic hydrogen from propylene to give ethane and allyl radicals.

The comparative data show that the increase in concentration of the azo compound increases slightly the extent of the coupling reaction. However, the decomposition of the *n*-butyl radicals to ethylene and ethyl radicals is still the dominant reaction.

1,1′-Azoisobutane.—The main gaseous products from the decomposition of 1,1′-azoisobutane are nitrogen, propylene and ethane with smaller amounts of methane, isobutane and isobutylene. The main reaction of the isobutyl radicals is decomposition to propylene and methyl radicals. Most of the methyl radicals dimerize to ethane. The percentage of methane is larger for this azo compound than that for 2,2′-azobutane where the main reaction is also decomposition of a butyl radical to propylene and methyl radicals. Methyl radicals may abstract hydrogen from propylene, isobutylene and isobutyl radicals. Since the data here are not sufficient to determine the extent of each of these reactions there is an uncertainty in the fraction of isobutyl radicals reacting by decomposition. This is reflected in the interpretation in Table IX. Since the influence of temperature and composition shows no significant trends because of this uncertainty, the comparative portion of Table IX has been omitted.

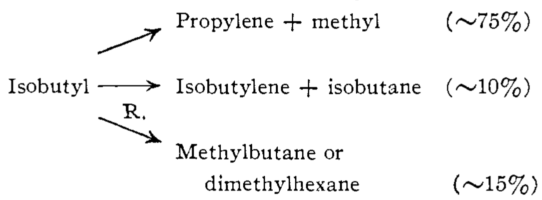
TABLE IX

DECOMPOSITION OF 1,1′-AZOISOBUTANE

Conditions, 1.2 % in helium at 445°

Gaseous products, mole %		Interpretation	
N_2	29	Isobutyl released	58 moles
CH_4	7	Disproportionation	6
C_2H_6	16	Decomposition	42–49
C_2H_4	0	Coupling	10–3
C_3H_8	0.7	Methyl released	42–49 moles
C_3H_6	42	Dimerization	32
i-C_4H_{10}	3	H-abstraction	7
i-C_4H_8	2	Coupling or addition	3–10

Reactions of isobutyl



Decomposition in Hydrogen.—More difficulty is encountered in the interpretation of the distribution of gaseous products from the decomposition in hydrogen than in helium. The increase in the ratio of saturated hydrocarbons to unsaturated hydrocarbons suggests hydrogenation of alkyl radicals with molecular hydrogen. The hydrogen

$$R\cdot + H_2 \longrightarrow R\text{-}H + H\cdot$$

atoms may then add to olefins or couple with other alkyl radicals.

These reactions along with those indicated for decomposition in helium will permit interpretations similar to those described above. However, more ambiguities arise and less confidence can be ascribed. For example, consider the data obtained for 1.2% 1,1-azoisobutane in hydrogen at 434°. The decomposition of 27 moles of azobutane releases 54 moles of isobutyl radicals. A carbon balance shows that there is 176 gram atoms of carbon in the C_1–C_4 products. Therefore, 40 gram atoms of carbon is assumed to be found in the C_5–C_8 products. A hydrogen balance on the gaseous products shows that the 176 gram atoms of carbon has been hydrogenated with an additional 58 gram atoms of hydrogen, an increase of 58/396 or 15% in hydrogen content.

Decomposition of isobutyl is the dominant reaction. The presence of 21 moles of propylene and 16 moles of propane requires the decomposition of at least 37 moles of isobutyl. The presence of 23 moles of methane and 5 moles of ethane requires at least 33 moles of methyl. The presence of 1 mole of isobutylene suggests the disproportionation of at least 2 moles of isobutyl. The additional 6 moles of isobutane requires hydrogen abstraction by isobutyl or reaction of isobutyl with atomic or molecular hydrogen. The propane may form by the addition of hydrogen atoms to propylene and subsequent hydrogenation of propyl radicals by atomic or molecular hydrogen.

The remaining 9 moles of isobutyl may be accounted for by a combination of several reactions but the extent of each is uncertain: (1) dimerization, (2) coupling with other alkyl radicals, (3) decomposition to propylene which is converted to allyl radicals, (4) disproportionation to isobutylene which is converted to methallyl radicals.

The data from the decomposition of 1.5% 2,2′-azobutane in hydrogen at 368° indicate that as 43 moles of azobutane decompose 86 moles of *sec*-butyl radicals are released. A carbon balance shows 59% of the carbon content is to be found in the C_5–C_8 products. A hydrogen balance on the gaseous products shows that there is an increase of 49/315 or 16% in hydrogen content. The presence of 20 moles of methane and 5 moles of ethane indicates that at least 30 moles of methyl radicals have been released. The presence of 2 moles of propane and 12 moles of propylene indicates the release of at least 14 moles of propylene. The amount of propylene should be the same as the amount of methyl, however. Therefore, at least 16 moles of propylene have been converted to allyl radicals which dimerize or couple. The presence of 2 moles of butenes indicates the disproportionation of 4 moles of *sec*-butyl. The presence of an additional 13 moles of *n*-butane suggests hydrogenation of *sec*-butyl by atomic or molecular hydrogen. This leaves no more than 39 moles of *sec*-butyl to dimerize or couple with radicals such as allyl, which adequately accounts for the 59% of the carbon content in the C_5–C_8 products. There is an uncertainty however because part of the 39 moles of *sec*-butyl could have decomposed to methyl and propylene, the methyl coupling with *sec*-butyl and the propylene being converted to allyl which then couples.

The data from the decomposition of 1,1′-azobutane in hydrogen show that decomposition of *n*-

butyl radicals to ethylene and ethyl radicals is the dominant reaction. The large amount of ethane cannot be accounted for only by dimerization of methyl. Hydrogenation of ethylene and ethyl radicals by atomic and molecular hydrogen is indicated. The presence of methane, propane and propylene suggests the decomposition of about one-tenth the *n*-butyl radicals to propylene and methyl radicals. Carbon balances show less than 17% of the carbon content in the C_5–C_8 products. Hydrogen balances on the gaseous products show an increase of 9-17% in hydrogen content.

Conclusion.—In the temperature range 200–450° azobutanes can be used as sources of free radicals. They decompose *via* first-order kinetics to give butyl radicals and nitrogen. However *n*-butyl, isobutyl and *sec*-butyl are unstable, easily decomposing to lower alkenes and alkyl radicals. If the isomeric butyl radicals as such are desired in a reaction, one must bear in mind this instability.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIF.]

Oxidation Inhibition by Diphenylamine

BY J. R. THOMAS AND C. A. TOLMAN

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A detailed study has been made of the inhibiting action of diphenylamine in the oxidation of cumene. Electron spin resonance has permitted the observation and identification of a relatively stable intermediate radical, diphenyl nitric oxide. Kinetic studies show that it is produced from a sequence of reactions between alkylperoxy radicals and diphenylamine which quantitatively follow the requirements of the Boozer–Hammond mechanism for oxidation inhibition. Critical rate constants are evaluated and limiting values are placed upon the equilibrium constant for the reversible reaction between cumylperoxy radical, diphenylamine and the complex species of the Boozer–Hammond mechanism.

The use of electron spin resonance has resulted in the observation and identification of the relatively stable intermediate radical, diphenylnitric oxide, when diphenylamine is used to inhibit the oxidation of hydrocarbons.[1,2,3] This paper presents the results of kinetic studies, made possible by e.s.r., which allow the inhibition mechanism to be specified in detail not previously possible.

Experimental

Diphenylnitric oxide was made by the method of Wieland.[4] It was purified by recrystallization from 50–50 ether and pentane. Tetraphenylhydrazine was prepared by the method of Wieland[5] or was material purchased from K and K Laboratories, Inc.

Oxidation Studies.—Oxidation studies were carried out in chlorobenzene solution at temperatures of 57.0 and 68.5°. The initiator used in all cases was azo-bis-isobutyronitrile (ABN). Oxygen absorption measurements were conducted in a stirred reactor in conjunction with a sensitive gasometer. The reactor, which also constituted the gas reservoir, was immersed in a carefully controlled water-bath. In cases where material was added to the reactor after the system was thermally equilibrated, a solution of the reagent was injected with a pipet through a controlled opening. All of the inhibitor studies were done this way, the inhibitor being added after the ABN-catalyzed oxidation rate had reached a steady value. Carefully done, this procedure caused very little upset to the system.

Electron spin resonance measurements were made with a Varian model 4500 spectrometer; 400 c.p.s. and 100 K.c.p.s. modulation were used at various times. The peak-to-peak height of the diphenylnitric oxide absorption band at low resolutions was used as a measure of concentration. The instrument was calibrated with samples of known concentration. All samples were thoroughly deoxygenated by alternate freezing and melting under vacuum. When diphenylnitric oxide reactions were studied in the absence of oxygen, they were sometimes done in sealed evacuated e.s.r. analysis tubes; at other times the reactions were conducted under nitrogen in conventional reactors from which samples were withdrawn at various times. If the samples, in e.s.r. analysis tubes, were not measured immediately they were stored in liquid nitrogen until they were analyzed.

Use of Diphenylnitric Oxide as a Radical Trap.—Diphenylnitric oxide is an attractive material to use as a radical counting material in many situations. While in the pure crystalline form it is considerably less stable than the commonly used α,α'-diphenylpicryl hydrazyl, its solutions are stable for prolonged periods of time. Even in solvents containing reactive hydrogen, such as cumene, its half-life at 100° is in excess of 50 hours. In addition, as is discussed below, it can be used reliably in the presence of oxygen under some conditions. Its disadvantages are the lack of stability of the crystalline material at room temperature and its lack of the intense color change upon reaction which is characteristic of DPPH. This latter characteristic renders the use of e.s.r. equipment preferable for its analysis in most situations.

Materials.—Cumene and chlorobenzene were Eastman Kodak Co. white label products; the latter was used without further purification, the former was passed through an alumina column.

Azo-bis-isobutyronitrile (ABN) and the diphenylamine were Eastman Kodak Co. products. The former was purified by recrystallization from methanol while the latter was recrystallized from hexane.

Results and Discussion

The basic problem of interest is the detailed mechanism of oxidation inhibition by diphenylamine. Since the radical, diphenylnitric oxide, has been found as a reaction intermediate, it must be suitably incorporated into a comprehensive mechanism. Furthermore, one would like to utilize the unique features of the radical's chemistry to verify various features of proposed inhibition mechanisms which have been supported largely by kinetic studies of the oxygen absorption reaction itself.

With these goals in mind the following discussion concerns itself with the chemistry of diphenylnitric oxide, *i.e.*, its reactions with alkyl and alkylperoxy radicals, and its behavior as an inhibitor. Next, the concentration behavior of the radical during the inhibition period is considered, with discussion of some experiments involving the competitive reactions of diphenylamine and diphenylnitric oxide with the oxidation chain propagating alkylper-

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(1) O. L. Harle and J. R. Thomas, *J. Am. Chem. Soc.*, **79**, 2973 (1957).

(2) J. R. Thomas, *ibid.*, **82**, 5955 (1960).

(3) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961).

(4) H. Wieland and M. Offenbacker, *Ber.*, **47**, 2111 (1914).

(5) H. Wieland and S. Gambarjan, *ibid.*, **39**, 1500 (1906).