

the most likely one is



which is endoergic by about 14 kcal./mole. It is possible, however, that the heat of reaction is zero or negative within the errors resulting from the uncertainties in measurements of appearance potentials, so that reaction 14 may indeed be energetically possible. But if we accept reactions 11 and 14, the calculated value of the molecular hydrogen yield per ion pair becomes 1.4, which is much larger than the experimental value of 0.9. And the value calculated should be a lower limit because molecular hydrogen is produced in most energetically favorable reactions between methane and ions other than  $\text{C}_2\text{H}_5^+$  and  $\text{CH}_5^+$ . To complicate matters further, molecular  $\text{H}_2$  is formed in the photolysis of  $\text{CH}_4$ .<sup>18</sup> Thus, one would expect the experimental molecular yield to be greater than

(18) B. H. Mahan and R. Mandel, *J. Chem. Phys.* (in press).

that calculated by Dorfman and Sauer. But it leaves unexplained the agreement between calculated and observed yields of  $\text{H}_2$  from  $\text{CH}_4$  found by them and the disagreement we find.

Polymers, usually of unknown composition, have been found among the products of the radiolysis of methane.<sup>2,19</sup> Our observation of numerous polymeric ions, which appear to react in consecutive fashion with the gas, suggests that one plausible mechanism of the polymerization process in gaseous methane is just these rather long chains of ion-molecule reactions. The measurements on the reaction cross sections and the pressure dependences of the intensities of the various polymeric species indicate that many of these ions react quite readily.

**Acknowledgments.**—The authors wish to thank Professor W. H. Hamill and Dr. F. H. Field for their valuable comments on this paper.

(19) R. W. Lampe, *J. Am. Chem. Soc.*, **79**, 1055 (1957).

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## Photoisomerization of 1,3,5-Cycloheptatriene and its Relation to Internal Conversion of Electronic Energy

BY R. SRINIVASAN

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The photolysis of 1,3,5-cycloheptatriene in the vapor phase led to the formation of toluene and bicyclo[3.2.0]heptadiene-2,6. The quantum yield for toluene increased with decreasing pressure, the extrapolated value at zero pressure being unity within experimental error. Inert gases such as helium, xenon, methane, carbon dioxide, nitric oxide, oxygen and diethyl ether affected the quantum yield in qualitatively the same way as pure cycloheptatriene but quantitatively their efficiencies seemed to fall in the order of their boiling points and molecular weights. In particular, xenon seemed to be much more efficient than helium as a quencher. The quantum yield for the formation of bicycloheptadiene was also pressure dependent, although the effect was small and the yield increased with an increase in pressure. Under the most favorable conditions only 5% or less of the excited cycloheptatriene molecules isomerized this way. It is suggested that isomerization to toluene occurs not from an electronically excited molecule of cycloheptatriene but from a vibrationally excited ground state molecule that is formed by the internal conversion of the electronic energy. In contrast, the formation of bicycloheptadiene is believed to occur from electronically excited cycloheptatriene.

### Introduction

The photolysis of 1,3,5-cycloheptatriene in diethyl ether solution has been studied by Dauben and Cargill.<sup>1</sup> The products they obtained were bicyclo[3.2.0]heptadiene-2,6, a small amount (2–5%) of toluene and a polymer. The formation of bicycloheptadiene from cycloheptatriene con-



stitutes a photoisomerization reaction which resembles the photodimerization of olefins to give cyclobutane derivatives.

The present investigation of the photolysis of cycloheptatriene in the vapor phase was conducted as part of a program of study of the photochemistry of simple aliphatic dienes and trienes.<sup>2</sup> In par-

(1) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961). The sample of cycloheptatriene used by these workers contained a small amount of toluene. Since they have not reported if the toluene found at the end of the photolysis was more than what was initially present, it is not known if toluene is formed during photolysis in solution.

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 5063 (1960); **83**, 2806 (1961).

ticular, it was of interest to see if reaction 1 will occur in the vapor phase since neither 1,3-butadiene nor 1,3-cyclohexadiene has been observed to undergo analogous photoisomerization reactions.<sup>2,3</sup>

### Experimental

Cycloheptatriene was obtained from the Chemical Procurement Laboratories (College Point 56, New York). It was fractionated on an 18' spinning band column of 23 theoretical plates. A small constant boiling fraction was collected, dried and admitted to the vacuum line. It was degassed and stored at Dry Ice temperature. Analysis by vapor phase chromatography showed that it contained traces of toluene and bicyclo[2.2.1]heptadiene-2,5 as impurities. It was found that neither compound interfered with the course of the photolysis of cycloheptatriene but a 2–4% correction had to be applied to the toluene yield that was obtained experimentally.

The following gases of reagent grade purity were obtained in sealed glass bulbs and used as such: helium, xenon and methane (Linde Co.); oxygen and carbon dioxide (Airco). Nitric oxide (Matheson Co.) was distilled from –156 to –195° before use. The diethyl ether used was the best analytical grade that was available. It was degassed before use.

A conventional high vacuum line in which the cycloheptatriene did not come in contact with stopcock grease

(3) R. J. de Kock, N. G. Minnard, and E. Havinga, *Rec. trav. chim.*, **79**, 922 (1960).

was used. The cylindrical reaction cell of quartz (4.4 cm. dia., 3.6 cm. long) was connected to a toeppler pump of three times its volume. In those experiments in which an inert gas was admitted into the cell along with the cycloheptatriene, repeated expansion of the mixture into the volume of the toeppler brought about the mixing of the two components.

The light source was a Hanovia 100 watt medium pressure mercury arc lamp. The quantum yields reported at 2600 Å. were obtained by the use of a Bausch and Lomb grating monochromator which admitted only the 2537 and 2652 Å. lines into the cell. The 3130 Å. radiation was obtained by the use of a Pyrex filter 2 mm. thick. At both wave lengths, diethyl ketone was used as the actinometer. In experiments in the presence of added gases, the full mercury arc was used in order to increase the intensity. The useful radiation extended from 2400 Å. below which the output of the lamp was small to 2800 Å. above which the quantum yields for the processes that were studied decreased by a factor of ten.

Although no polymer was detected on the windows of the cell after the photolysis of cycloheptatriene to low conversion, the cell was detached from the line at the end of every third experiment and cleaned with an oxidizing mixture of acids, washed with water, dried and resealed to the line.

Photolysis of cycloheptatriene gave rise to only trace amounts of gaseous products. All of the material that was condensable at  $-195^{\circ}$  was introduced into a Perkin-Elmer gas chromatograph fitted with a two-meter polypropylene glycol column maintained at  $70^{\circ}$ . Two peaks due to the products of photolysis were observed. The first which was always small was found to be due to bicyclo[3.2.0]heptadiene-2,6 by comparison with the retention time of the authentic sample.<sup>4</sup> The second peak, which was the major one, was due to toluene as shown by comparison of its infrared spectrum and its retention time with that of an authentic sample.

Quantitative analysis for bicycloheptadiene and toluene was made by estimating the area under the peaks in the gas chromatogram. The detector in the instrument was calibrated with pure vapor samples of each product. The analysis for toluene at high (>17 mm.) pressures of cycloheptatriene was satisfactory to only  $\pm 25\%$  but at lower initial pressures of the triene an accuracy of  $\pm 10\%$  was obtainable over a period of time.

## Results

**1. Quantum Yields at 2600 Å.**—At 15 mm. pressure of cycloheptatriene at room temperature, the quantum yields for the formation of toluene and bicycloheptadiene were 0.29 and 0.008, respectively. Both showed a dependence on the pressure of cycloheptatriene. The plot of  $1/\Phi_{\text{toluene}}$  versus pressure (Fig. 1) was a satisfactory straight line. The best fit of the experimental points gave a value of  $1.12 \pm 0.30$  for the intercept. In contrast, the quantum yield for bicycloheptadiene increased with an increase in pressure, the extreme values being 0.0036 (6.2 mm.) and 0.010 (22.1 mm.).

**2. Influence of Added Gases at 2600 Å.**—The influence of various gases on the quantum yields for toluene and bicycloheptadiene at room temperature are shown in Table I. The product yields are proportional to the quantum yield since the useful radiation was totally absorbed. The pressure of cycloheptatriene was kept as close to a value of 15 mm. as possible, but in order to calculate the efficiency of the added gas in decreasing the yield of toluene, the toluene yield at the actual pressure of cycloheptatriene that was used was taken into account. The last column gives the ratio of the yield of toluene in the absence of the inert gas,

(4) Prepared by the photolysis of cycloheptatriene in ether solution according to ref. 1. The author wishes to thank Professor William G. Dauben for making the infrared spectrum of bicycloheptadiene available to him for comparison.

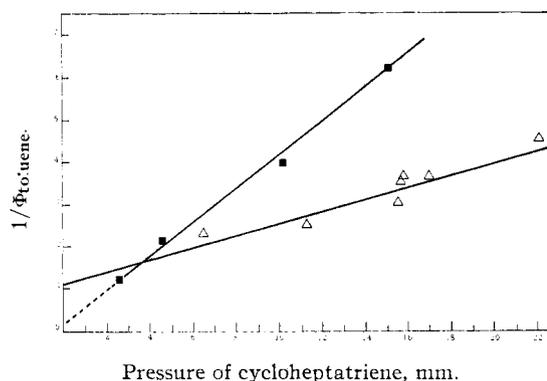


Fig. 1.—Plot of  $1/\Phi_{\text{toluene}}$  vs. pressure at room temperature:  $\Delta$ , values at 2600 Å.,  $\blacksquare$  at 3130 Å. Multiply ordinate by 10 for use at 3130 Å.

$(A_{\text{toluene}})_0$  to the yield in the presence of the inert gas ( $A_{\text{toluene}}$ ). In Fig. 2, this ratio is plotted as a function of the pressure of the inert gas in six cases. By definition, the origin is also a point on each of these lines. It is seen that a satisfactory straight line plot is observed in nearly all cases. The slopes of these lines are given in Table II.

TABLE I  
EFFECT OF ADDED GASES ON THE PHOTOLYSIS OF  
CYCLOHEPTATRIENE AT 2600 Å.

Average  $C_7H_8$  pressure 14.7 mm.; time 5 min.; room temp. cell vol. 54.7 ml; unfiltered medium pressure Hg arc.

Gas added	Gas press., mm.	Bicycloheptadiene Toluene		$(A_{\text{toluene}})_0 / (A_{\text{toluene}})$
		μmole		
Helium	67.6	0.18	6.82	1.11
	112.6	.20	6.32	1.15
	171.5	.24	5.25	1.36
	212.5	.24	5.48	1.35
Xenon	65.0	.16	6.63	1.17
	123.1	.16	5.75	1.27
	178.7	.20	5.34	1.36
	285.1	.16	4.07	1.81
Methane	324.6	.16	3.59	1.99
	62.3	.27	5.12	1.41
	90.5	.25	4.27	1.83
	141.1	.30	3.74	2.00
Oxygen	26.5	.20	6.35	1.06
	38.4	.18	6.97	1.08
	57.6	.19	6.71	1.11
	120.6	.19	5.14	1.56
Nitric oxide	280.9	.21	4.13	1.80
	50.8	.13	4.78	1.53
	119.2	.17	4.96	1.35
Carbon dioxide	41.5	.21	5.35	1.34
	83.8	.22	4.04	1.81
	141.4	.20	3.70	1.94
	208.8	.30	2.76	2.45
Diethyl ether	27.3	.25	4.69	1.65
	55.8	.33	3.26	2.34
	83.4	.35	2.60	2.94
	108.2	.35	2.06	3.69

**3. Influence of Temperature at 2600 Å.**—The influence of temperature on the yields of toluene and bicycloheptadiene is shown in Table III. The product yields are again directly proportional to the quantum yields.

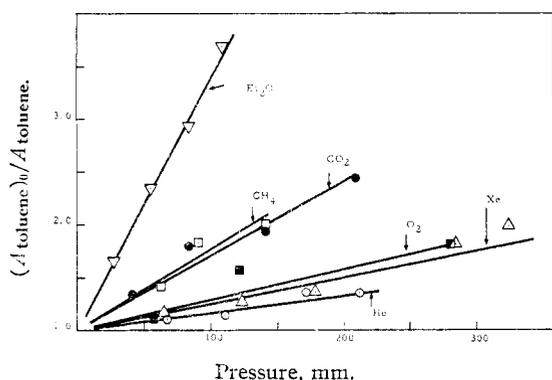


Fig. 2.— $(A_{\text{toluene}})_0/A_{\text{toluene}}$  vs. pressure of inert gas at room temperature:  $\circ$ , helium,  $\nabla$  xenon,  $\blacksquare$  oxygen,  $\bullet$  carbon dioxide,  $\square$  methane,  $\nabla$  diethyl ether.

4. Quantum Yields at 3130 Å.—Quantum yields for the formation of toluene and bicycloheptadiene at 3130 Å. at room temperature are listed in Table IV. The effects of a change in cycloheptatriene pressure and of the addition of carbon dioxide are shown. A plot of  $1/\Phi_{\text{toluene}}$  versus the pressure of cycloheptatriene (without any added gas) is included in Fig. 1. Although the experimental points fall on a satisfactory straight line, the extrapolation to the Y-axis to obtain an intercept is long and hence unreliable.

TABLE II  
RELATIVE EFFICIENCIES OF INERT GASES IN QUENCHING THE FORMATION OF TOLUENE (Pressure to pressure basis)

Gas added	Pressure range, mm.	Efficiency
Helium	0-212.5	0.13
Xenon	0-324.6	.19
Oxygen	0-280.9	.23
Carbon dioxide	0-208.8	.56
Methane	0-141.1	.60
Ether	0-108.2	1.93

TABLE III  
EFFECT OF TEMPERATURE ON THE PHOTOLYSIS OF CYCLOHEPTADIENE (For conditions see Table I)

Pressure of $C_7H_8$ , mm.	Concentration, mole/l. $\times 10^4$	Temp., °C.	Bicycloheptadiene	
			$\mu\text{mole}$	
12.4	6.628	27.0	0.16	8.44
14.3	6.845	62.0	.14	8.61
16.1	6.769	108.3	.13	9.47
18.8	6.916	162.8	.06	9.54 <sup>a</sup>

<sup>a</sup> Not cleanly separated from cycloheptatriene by gas chromatography.

### Discussion

**Nature of the Excited State.**—The first absorption region in the ultraviolet spectrum of cycloheptatriene extends from about 3300 to 2250 Å. The absorption is intense ( $\log \epsilon_{\text{max}} = 3.62$ ) which when coupled with the fact that the ground state is a singlet, suggests that the excited state that is formed is also a singlet. Integration of the area under the absorption curve indicates a value of

TABLE IV

### PHOTOLYSIS OF CYCLOHEPTADIENE AT 3130 Å.

Medium pressure Hg arc; 2 mm. Pyrex filter, room temperature, cell vol. 54.7 ml.; incident intensity  $1.87 \times 10^{16}$  Q/sec.

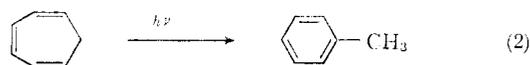
Pressure $C_7H_8$ , mm.	Gas added	Gas pressure, mm.	Time, min.	$\Phi_{\text{BCH}}^a$	$\Phi_{\text{toluene}}$
15.1	..	...	186	0.0015	0.016
10.2	..	...	180	.0016	.025
4.6	..	...	120	.0014	.046
2.6	..	...	90	.0013	.081
14.6	CO <sub>2</sub>	68.9	184	.0016	.010
14.5	CO <sub>2</sub>	152.5	180	.0016	.007

<sup>a</sup> Quantum yield of bicycloheptadiene.

about  $10^{-9}$  sec. for the lifetime of the excited molecules.

In the present study, two isomeric products were obtained on irradiation of cycloheptatriene. The formation of neither was totally quenched by the addition of even considerable amounts of oxygen or nitric oxide. This can be interpreted to mean that (i) the isomeric products are formed by intramolecular rearrangement processes and (ii) the isomerization reactions may not arise from a triplet excited state of cycloheptatriene. Although no light emission from cycloheptatriene was observed visually when it was subjected to ultraviolet irradiation, it was not established that no light was emitted at all under these conditions. Hence, for the purpose of this discussion it will be assumed that the photochemistry of cycloheptatriene in the wave length region from 2600 to 3130 Å. involves only one electronically excited state—an upper singlet.

**Formation of Toluene.**—The isomerization reac-



tion 2 is the predominant process at the pressures used. This photoisomerization has not been reported before in the gas phase or in solution. The plot of  $1/\Phi_{\text{toluene}}$  vs. pressure shows that at zero pressure almost all of the photons absorbed by cycloheptatriene will lead to this reaction. The nature of the excited cycloheptatriene molecule which participates in (2) is indicated by the effect of pressure on the formation of toluene. The excitation energy involved must be such that diverse molecules from helium to diethyl ether can remove this energy through collisions. Although both electronic and vibrational energy may be removed in collisional processes, a greater sensitivity to the nature of the colliding molecule is expected for the transfer of electronic energy. The data in Table II show that the efficiencies of the various gases in quenching reaction 2 increase according to their molecular weights and boiling points, a trend which suggests very little specificity. In particular, the fact that xenon is more efficient than helium, although they both contain all of their electrons in closed shells, seems definitely not in favor of the idea of the transfer of electronic energy in the deactivating process.

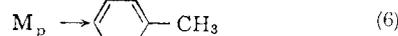
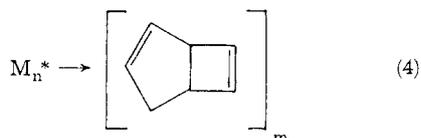
The influence of an increase in temperature which is observed to promote the formation of toluene

reinforces the idea that the addition of vibrational energy to cycloheptatriene favors reaction 2.

It is postulated that *the formation of toluene occurs from a high vibrational level of the ground electronic state of cycloheptatriene and not from the upper electronic state.* The basis for this postulate will be discussed later.

**Formation of Bicycloheptadiene.**—The formation of bicycloheptadiene, which is the first reported instance of the photochemical synthesis of a cyclobutene in the vapor phase, appears to account for less than 5% of the photons absorbed by cycloheptatriene under all experimentally realizable conditions. The increase in quantum yield that is caused by an increase in pressure that is seen at low pressure seems to level off at high pressure as may be noted from the effect of diethyl ether on the yield (Table II). This slight effect may be interpreted to mean that a loss of vibrational energy in the electronically excited state of cycloheptatriene favors reaction 1 but the results at 3130 Å. contradict this. At this wave length, although the vibrational energy of the excited molecule must be less than at 2600 Å., the quantum yield of bicycloheptadiene also decreases. Since in the ground electronic state, reaction (1) is not known whereas the reverse of (1) does occur,<sup>1</sup> the effect of a change in pressure on the photochemical formation of bicycloheptadiene may be explained as follows: reaction 1 may lead to a "hot" bicycloheptadiene which, unless it loses its excess vibrational energy in collisions in a short time, will revert to cycloheptatriene. This would also fit in with the decrease in the yield of bicycloheptadiene with an increase in temperature.

**Details of the Photochemical Processes.**—The reactions that occur in this system on absorption of light may be represented as:



M stands for cycloheptatriene. The asterisk denotes electronic excitation while the subscripts m, n, and p represent vibrational levels much higher than the zeroth level. For the sake of simplicity a bimolecular reaction to represent the deactivation of "hot" bicycloheptadiene has not been included.

The basis for the postulate that the formation of toluene occurs from  $M_p$  rather than  $M_n^*$  will be examined here. It is possible that the decrease in the quantum yield of toluene with an increase in pressure is due to a loss in the vibrational energy of the molecule in the upper electronic state. The quantum yield of toluene at 3130 Å. which is

lower than the value at 2600 Å. may be interpreted to support this idea. But against this explanation it can be pointed out that: (i) The formation of bicycloheptadiene does not show the same effect. Since only one electronically excited state is assumed to be involved in both processes, the two should show the same pressure dependence if they occur from identical states.

(ii) It is unlikely that collisional loss of energy occurs at all in the upper electronic state since its lifetime is only of the order of  $10^{-9}$  sec. The interval between collisions at the pressures used is 1–10 times greater than this value.<sup>5</sup> It is more likely that the pressure effects that are observed arise from vibrationally excited ground state molecules.

It is known that cycloheptatriene rearranges to toluene under the action of heat.<sup>6</sup> In this system, the electronically excited molecules of cycloheptatriene may internally convert their energy to give vibrationally excited molecules in the ground electronic state. Unless the excess vibrational energy is rapidly removed in collisions, these molecules will rearrange to give toluene. At zero pressure the latter will be virtually the only process occurring in the system. Even at as high as 6 mm. pressure, 45% of the excited cycloheptatriene molecules follow this path. In line with this reasoning, photolysis in solution leads to mostly bicycloheptadiene and very little toluene.<sup>1,7</sup>

The mechanism that is proposed here already has been suggested by Franck and Sponer<sup>8</sup> as a plausible one in the photochemistry of many compounds which decompose by identical reactions both thermally and photochemically.

The relationship between the upper singlet state and the ground state must be such in cycloheptatriene that internal conversion may occur as easily in the high vibrational levels in the upper state as in the lower vibrational levels. This would explain the fact that the plot of  $1/\Phi_{\text{toluene}}$  vs. pressure extrapolates to unity at both 2600 and 3130 Å., although the uncertainty is large in the latter instance.

A further interesting point is that the slope for the plot of  $1/\Phi_{\text{toluene}}$  vs. pressure is greater at 3130 Å. than at 2600 Å. This is true for both the pure hydrocarbon (Fig. 1) and for the addition of carbon dioxide. If the deactivation step 7 caused the loss of all of the excess vibrational energy in one collision (as the reaction has been written), the slopes of the plots should be independent of the excess vibrational energy possessed by the excited molecule, *i.e.*, the slopes should be the same at

(5) The occurrence of long range energy transfer in this system would vitiate this argument as the effective lifetime of the excited state would then be longer than the calculated value. Experiments on the photolysis of cycloheptatriene ( $p = 13.4$  mm.) in the presence of aniline ( $p = 0.4$  mm.) showed that the presence of aniline did not affect the yield of toluene. Hence the question of long range energy transfer need not be considered further.

(6) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); this result was confirmed in the present study by pyrolysis of cycloheptatriene in a 200 ml. Pyrex bulb of 3.73 cm. radius,  $p = 50$  mm.,  $T = 460$ ;  $t = 10$  min. Toluene was the only important product.

(7) R. Srinivasan, unpublished work.

(8) J. Franck and H. Sponer, "Volume Commemoratif V. Henri," *Maison Desoer, Liege, Belgium*, 1948, p. 169.

both wave lengths.<sup>9</sup> The difference in slopes that is observed clearly shows that several collisions are required before the vibrationally excited molecule

(9) This statement does not take into account the change in the microscopic isomerization rate with increasing vibrational energy. However, calculations show that the observed difference in slopes cannot be wholly accounted for by such an effect alone, and that it is

loses enough energy to prevent it from participating in reaction 6.

**Acknowledgment.**—The author wishes to thank Dr. Harold L. Friedman for his advice and encouragement during the course of this work.

probably a combination of this effect and weak collisional interactions that actually exists.

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## Factors Controlling the Rate of Electron Transfer. I. The Effect of Halogen Substitution in Organic Mediators<sup>1</sup>

By R. T. M. FRASER<sup>2</sup>

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A kinetic study has been made of the reduction by  $\text{Cr}^{++}$ ,  $\text{V}^{++}$  or  $\text{Eu}^{++}$  of complex ions of the type  $(\text{NH}_3)_5\text{Co}(\text{III})\text{L}$ , where L is a halogen derivative of acetic, benzoic or fumaric acid. With the acetato and benzoato complexes, the rate of chromous ion reduction decreases as the size of the substituent increases. Changes in opposite directions in  $\Delta S^\ddagger$  in chromous and vanadous reactions are interpreted in terms of substitution labilities of the reductants. Substitution of  $-\text{CO}_2\text{H}$  in the 2-position of the ligand catalyzes reduction by  $\text{V}^{++}$  and  $\text{Eu}^{++}$ ;  $-\text{OH}$  in the 2-position catalyzes reduction by  $\text{Cr}^{++}$ . The role of halogen substitution in fumaric acid is more complex, but can be related both to the size of the halogen and its electromeric effect. All three reductants react by inner-sphere (bridged) activated complexes.

### Introduction

The chromous ion reduction of pentammine cobalt(III) complexes has recently been studied in some detail.<sup>3</sup> Besides attack by the reductant at the carboxyl bound to the cobalt, attack at a remote  $-\text{CO}_2\text{R}$  group with electron transfer through the (conjugated) ligand has been demonstrated. This paper reports the results of substituting halogen for hydrogen in the ligand: in the acetates and benzoates the carbon involved in halogenation is not a participant in the electron transfer path, while in the fumarates the halogen is attached to carbon situated between the cobalt center and the remote carboxyl. Although the rate of reaction is changed only slightly, there are striking alterations in the reaction paths for the reduction as the position of halogenation is varied.

### Experimental

**Chemicals. Compounds Used as Ligands.**—The carboxylic acids used were the purest grade available from Distillation Products Industries or from the Fisher Scientific Co., except 4-cyanobenzoic acid and chloromaleic anhydride (The Aldrich Chemical Co.). Chlorofumaric acid was prepared from chloromaleic anhydride by heating with excess hydrochloric acid on a water-bath. To prepare bromo- and iodofumaric acids, the corresponding hydrogen halide and acetylenedicarboxylic acid were mixed in water, allowed to stand, dried and recrystallized. Dichloro- and dibromofumaric acid were prepared by the action of chlorine or bromine on an aqueous solution of acetylenedicarboxylic acid at 0°. Diiodofumaric acid was prepared by the method of Eichelberger.<sup>4</sup>

The method for preparation of the pentammine cobalt(III) complexes has been described elsewhere.<sup>3</sup>

**Reductants.**—Solutions containing chromic, europic or vanadyl perchlorate and perchloric acid were reduced over amalgamated zinc and stored under nitrogen until required. The stock solution of vanadyl perchlorate was prepared from vanadyl sulfate and barium perchlorate. Europic perchlorate solution was obtained by dissolving 99%

europium oxide (Allied Chemical Corporation, Trona brand, code 1012) in perchloric acid, filtering and diluting with water. The sodium perchlorate solution used to adjust the ionic strength of solutions to 1.0 was prepared by mixing equivalent amounts of A.R. sodium hydroxide and perchloric acid.

**Kinetic Measurements.**—The solutions of the pentammine cobalt(III) complexes and the reductants were either mixed by a stream of nitrogen, then transferred under nitrogen to the 10-cm. optical cells, or the complex solution was degassed directly in the cells (fitted with serum caps), and the reductant then added from a syringe. Both methods gave the same rate constants. The rate of reaction was studied by following the rate of disappearance of the 500 m $\mu$  absorption maximum of the cobalt complex. Three spectrophotometers were used in the course of this work: a Beckman DK1 recording spectrophotometer, a Beckman DK2 and a Perkin-Elmer 350. The method for analysis of the rate plots to yield specific rate constants has been described previously.<sup>3</sup> Infrared spectra were measured on a Perkin-Elmer Infracord.

**Analysis of Complexes.**—The nitrogen content of the pentammine cobalt complexes was determined by the modified Kjeldahl method of Horan and Eppig.<sup>5</sup> Experiment showed that the reproducibility was better than 2%.

The perchlorate content of the complexes was determined by precipitation with tetraphenylarsonium chloride. The acid equivalent of each complex was determined by titration with standard base,<sup>3</sup> using a Phillips 9400 pH meter equipped with an Ingold combination electrode (No. 404).

**Reduction in O<sup>18</sup>-Enriched Water.**—The succinate complex ( $1 \times 10^{-4}$  mole) was dissolved in 10 cc. of enriched water (1.6% D<sub>2</sub>O<sup>18</sup>: The Isomet Corporation); acid and water (total added = 0.5 cc.) were added to bring the  $[\text{H}^+]$  to 0.2 or 0.6 M, then 1 cc. of 0.1 M vanadous ion was added. The solution was stirred with nitrogen for 30 minutes, extracted with ether for 4 hr. and the extract dried over anhydrous sodium sulfate for 24 hr. After removal of the ether by warming, the dried residue was dissolved in sodium carbonate solution, then acidified and re-extracted with ether. The product was analyzed for O<sup>18</sup> content by the method of Anbar and Guttman.<sup>6</sup>

### Results

**1. Reactions Independent of Hydrogen Ion Concentration.**—All these reactions obeyed the rate law

$$-d(\text{CoL}^{++})/dt = k(\text{CoL}^{++})(\text{reductant})$$

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