phatics is equally well established by experiment. An explanation for the anomalous results reported here is that the resonance stabilization of triarylmethyls is accompanied with an increase of diamagnetism perpendicular to the rings, in other words, with an increase of molecular anisotropy in the free radicals. An explanation of this sort has been suggested by Wheland.[10]

If this explanation is correct, then it is clear why neither Pascal's constants nor a measurement on the corresponding methane can ever give the true diamagnetic correction. Neither the Pascal's constants method nor the methane method are structurally comparable to the free radical itself because the additional electronic currents are ignored in the one case, absent in the other.

In order to explain the results observed in this work, it is necessary to assume that the diamagnetic correction has been underestimated by from 65 to 120%. If an enhancement of diamagnetism actually occurs it is likely to be only in the direction perpendicular to the plane of the rings. The observed results could, therefore, be explained on the basis of a 195 to 360% increase in the principal molecular susceptibility normal to the plane of the rings. This increase is large, and unfortunately there seems to be available no method by which the electronic currents may be estimated in the resonating bonds joining the rings to the methyl carbon. There is as yet no magnetic theory for aliphatic conjugation, and this is essentially the problem involved. However, it is to be noted that a 300% anisotropy is by no means unusual. In fact, this is approximately the anisotropy produced in benzene itself by one resonating electron. If one free electron may be thought of as circulating around the whole structure of any triarylmethyl, then it is easy to imagine such a substantial increase of diamagnetism. Further support for this explanation is gained from the decrease of the necessary diamagnetic increment with increasing temperature. It is well known that resonance produced diamagnetic anisotropy is diminished with rising temperature.

It will be noted that this explanation serves for the anomaly previously mentioned in connection with the Chichibabin hydrocarbon. If the diamagnetic correction is thus underestimated it becomes clear why a direct susceptibility measurement on this hydrocarbon could be interpreted as indicating no dissociation, while an *ortho–para* hydrogen determination which involves no diamagnetic correction could yield a more accurate result.

It is somewhat more difficult to explain the reported 100% dissociation of hexa-*p*-biphenylethane in the solid. Possibly the fitting of the free radical molecules into the crystal lattice involves sufficient distortion to reduce the electronic currents and hence the molecular anisotropy. But it is not clear if this could be done and yet leave sufficient resonance energy to stabilize the radical.

It is a pleasure to acknowledge the support of the United States Rubber Company in connection with this work.

Summary

Magnetic susceptibility measurements on toluene solutions of hexa-*p*-biphenylethane and hexa-*p*-*t*-butylphenylethane suggest that resonance stabilization of triarylmethyls is accompanied by a substantial increase of molecular diamagnetism. This observation throws some doubt on quantitative magnetic studies on free radicals.

EVANSTON, ILLINOIS RECEIVED JANUARY 28, 1950

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[10] G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 696.

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

Photochemical Studies. XLIII. Propiolactone[1]

BY ROBERT H. LINNELL AND W. ALBERT NOYES, JR.

The photochemical decomposition of β-propiolactone does not seem to have been investigated previously. Data essential for establishing the details of the mechanism could not be obtained for this compound. Its vapor pressure at 51° is only 10 mm. so that studies of the vapor could not be made without using higher temperatures. Polymerization and other thermal reactions make the compound unstable under such conditions. The photochemical data were obtained by irradiation of the liquid.

Experimental

The β-propiolactone was obtained from the B. F. Goodrich Company and was synthesized from ketene and formaldehyde.[2] It polymerizes slowly at room temperature but can be kept satisfactorily at 5° or below. The physical properties have been listed.[3] The material used in these experiments was vacuum distilled from a temperature of 25° and condensed at 0°, the middle fraction was retained, and it was stored at 0°; $n^{25}\mathrm{D}$ 1.4104, lit. 1.4110.[3]

Chloroform used as a solvent for obtaining the absorp-

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[1] This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

[2] F. E. Küng, U. S. Patent 2,356,459 (1944); T. R. Steadman, *ibid.*, 2,424,589 (1947); T. R. Steadman and P. L. Breyfogle, *ibid.*, 2,424,590 (1947).

[3] T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948).

tion spectrum of the lactone was washed with sodium carbonate, with distilled water, and was dried by anhydrous calcium chloride for three hours. It was distilled through a "Purdue" column with a reflux ratio of 2:1, and the fraction boiling 62.3–62.4° was retained.

Customary procedures for uranyl oxalate and potassium permanganate solutions were used.[4] A quantum yield of 0.62 was assumed for the uranyl oxalate actinometer.[4] Since the quantum yields were very low and represent only orders of magnitude, the solutions were not stirred.

The light source was a Hanovia SC-2537 "end-on" mercury resonance lamp. Light intensities were varied by neutral density filters.[5] These filters cannot be considered as neutral for short wave lengths, and their interposition decreases the intensity of 1849 Å. radiation relative to 2537 Å. radiation.

The photolyses were carried out in pure liquid β-propiolactone. Chloroform was not suitable as a solvent for the photochemical experiments because of its considerable absorption at 2537 Å.

Gaseous products were removed by Toepler pumps after freezing the lactone either with liquid nitrogen, with pentane mush, or with Dry Ice-alcohol mixtures. The lactone was distilled several times to liberate gaseous products, and products were removed after each distillation. In some of the initial high intensity runs the gas uncondensed by liquid nitrogen was absorbed by cosorbent.[6] This showed carbon monoxide to be the only gas uncondensed by liquid nitrogen. These results were checked by combustion over copper oxide.[8] The fraction volatile at −130° was shown to be a mixture of carbon dioxide and ethylene both by the Blacet–Leighton technique[7] and by combustion with oxygen over a hot platinum wire.[8] Acetaldehyde was identified in the fraction volatile at Dry Ice temperatures by comparison of the infrared spectrum with that of a known sample. Semi-quantitative data on the amount of acetaldehyde were obtained by a colorimetric method using *p*-hydroxybiphenyl.[9] Absorption in the infrared identified as due to ethylene and acetylene was also found in the fraction volatile at Dry Ice temperatures obtained in one long run made to accumulate appreciable quantities of products.

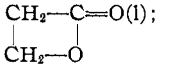
The reaction cell was 26 mm. in diameter, 5 mm. in internal thickness, and fuzed quartz windows were approximately 1 mm. in thickness.

Combustion data were obtained with an Emerson Bomb Calorimeter, and benzoic acid obtained from the Bureau of Standards was used as a standard. Infrared spectra were obtained with a Perkin-Elmer model 12B infrared spectrograph, and ultraviolet absorption curves were obtained with a Beckman quartz spectrophotometer.

Results

(a) **Heat of Combustion.**—Temperature rise: 1.999 ± 0.004 degrees/g. (av. of four determinations). Temperature rise: 2.604 ± 0.033 degrees per gram of benzoic acid. Corrections for nitric acid formation, electrical energy, combustion of wire were negligible. Heat of combustion of benzoic acid: 6315 cal./g. Heat of combustion of β-propiolactone: (1.999/2.604) ×. 6315 × 72.04 = 349000 ± 7000 cal./mole. The heat of formation is given by

$$3C(gr.) + 2H_2(g) + O_2(g) =$$



$$\begin{array}{l} CH_2\text{—}C{=}O(l); \\ \;| \qquad\;\; | \\ CH_2\text{—}O \end{array}$$

$$\Delta H^{\circ}_{298} = -71000 \text{ cal.} \quad (1)$$

All expected photochemical reactions of β-propiolactone are either exothermic or thermoneutral.

(b) **Ultraviolet Absorption.**—Chloroform proved to be the only solvent tried which could be used for determination of the absorption spectrum of β-propiolactone. It absorbs so strongly at 2537 that it could not be used in the photochemical experiments. Absorption data to rounded wave lengths are given in Table I.

TABLE I

ULTRAVIOLET ABSORPTION OF β-PROPIOLACTONE

Transmission of Solution/Transmission of $CHCl_3$, 1-cm. cell, 25°

Concn., g./l.	2800 Å.	2700 Å.	2600 Å.	2500 Å.
43.7	0.87	0.74	0.57	0.43
84.3	0.66	0.50	0.33	0.17

(c) **Infrared Data.**—The lactone showed strong infrared absorption at 5.45 ± 0.02 μ in the liquid phase and at 5.36 ± 0.01 μ in the gas phase. These correspond to 1835 and 1866 cm.$^{-1}$, respectively. Both are probably due to the carbonyl frequency, although they are higher than in esters and ketones.

(d) **Polymer.**—During long exposure the lactone assumed a light yellow color. The undecomposed lactone could be pumped off leaving a light yellow residue. This residue showed an infrared absorption at 5.75 μ or 1739 cm.$^{-1}$. This frequency is approximately the same as carbonyl frequencies in esters. Ultraviolet absorption of

TABLE II

QUANTUM YIELDS OF FORMATION OF GASEOUS PRODUCTS FROM LIQUID β-PROPIOLACTONE

Absorbed incident intensity einsteins/sq.cm./min. × 10^7	Quantum yields × 10^3 CO	CO_2	C_2H_4
Unfiltered Radiation (T = 25°)			
1.07	41	5.0	1.8
1.00	45	7.5	2.4
1.06	35	7.4	2.3
0.94	38	7.1	...
0.207	20	10.0	2.0
0.688	28	15	2.6
0.630	28	8.3	1.6
0.217	19	10	1.2
0.217	17	9.0	1.5
1.60[a]	64	..	...
1.60[a]	41	..	...
1.60[a]	30	..	...
1.60[a]	19	..	...
Unfiltered Radiation (T = 0°)			
0.207	22	8.0	2.5
0.207	21	8.5	1.3
1.17	51	10	5.4
1.04	45	9.4	2.6
1.04	42	11	2.7
Evacuated Filter Cell (T = 25°)			
1.3	39	12	2.2
1.3	41	11	3.1
Filter Cell Filled with 1 M CH_3CO_2H (T = 25°)			
1.1	5.0	7	...
1.3	4.6	13	1
1.3	3.9	7	1
Filter Cell Filled with Water (T = 25°)			
1.4	5.7	7	1

[a] These four successive runs were made without cleaning the windows to show the effect of polymer formation.

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[4] W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

[5] See R. Gomer and W. A. Noyes, Jr., *ibid.*, **71**, 3390 (1949).

[6] Burrell Technical Supply Co., Pittsburgh, Pennsylvania.

[7] F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931); **5**, 272 (1933); **6**, 334 (1934).

[8] W. M. Manning, THIS JOURNAL, **56**, 2589 (1934).

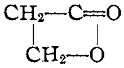
[9] E. H. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).

lactone which had been exposed to radiation showed no characteristic peaks but a considerably enhanced absorption of the same general form as the lactone itself. Microanalyses of the polymer were not very consistent, probably because of its hygroscopic nature, but they showed that the empirical formula was within the experimental error of the same as for the monomer. The analytical results do not exclude the possibility that some ethylene was incorporated in the polymer.

(e) **Gaseous Products.**—The gaseous products which were positively identified are: CO, CO_2, C_2H_4, CH_3CHO. Quantum yields of formation of these various products are shown in Table II. The transmission of the windows of the cell was reduced approximately 20% by deposition of the polymer. The transmission was measured before and after each run, and a mean value of the transmitted intensity used in the calculation. About 10% of the radiation from the lamp was absorbed by the actinometer and not absorbed by the lactone. A correction was made for this in the calculation.

Discussion

Three over-all reactions of β-propiolactone (in addition to polymerization) may be visualized



$$\begin{array}{l} CH_2\text{—}C{=}O \\ |\qquad\ | \\ CH_2\text{—}O \end{array}$$

$$(l) = CO_2(g) + C_2H_4(g) \qquad (2)$$

$$= CO(g) + CH_3CHO(g) \qquad (3)$$

$$= CH_2{=}CHCO_2H(l) \qquad (4)$$

Ample energy is provided by 2537 Å. radiation to cause any of these reactions to take place.

The data with unfiltered radiation indicate an apparent variation of the ratio CO/CO_2 with intensity. This was found to be due to the variation in the ratio of intensities of the 2537 and 1849 lines caused by the "neutral density" filters. A precise estimate of the intensity of 1849 radiation was not possible, but the carbon monoxide quantum yield at that wave length is high and may approach unity. The carbon dioxide quantum yield was about the same with and without the acetic acid filter (which removed 1849) and was independent of intensity.

The formation of either carbon monoxide or carbon dioxide involves rupture of the ring in two places. The very slight effect of temperature lends support to the view that reactions (2) and (3) are both primary processes. The formation of acetaldehyde involves the shift of a hydrogen atom from one carbon atom to another, a process which can occur quite easily in the liquid phase and which may occur apparently even in the gas phase under some conditions.[10]

The quantum yield of acetaldehyde formation could not be obtained precisely, but it was at least approximately the same as the quantum yield of carbon monoxide formation. The data in Table II show, however, that the yield of ethylene was always inferior to the yield of carbon dioxide. This may be due to the incorporation of ethylene in the polymer. Some experiments were performed with added ethylene. Visual observation indicated an enhanced rate of polymer formation in these experiments.

The normal polymer of the lactone should be a polyester acid and should be either a colorless oil or a white solid.[3] The polymer formed photochemically shows infrared absorption characteristic of esters, but it has a light yellow color. Acetylene was identified in the gases obtained from a long run by infrared band at 13.76 μ,[11] and this may come from photosensitized decomposition of the ethylene. The latter is usually accompanied by some polymerization yielding cuprene. Some of the polymer formed on the windows in these experiments had the characteristics of cuprene.

It may be concluded, therefore, that β-propiolactone at 2537 Å. behaves partially in the same manner as cyclic ketones and partly as an acid anhydride. Little more can be said about the mechanism of the reaction than this. No evidence for or against reaction (4) was obtained.

Summary

1. The heat of combustion of liquid β-propiolactone is 349 ± 7 kcal. per mole.

2. At 2537 Å., CO, CO_2, C_2H_4 and CH_3CHO are formed photochemically by irradiation of liquid β-propiolactone with yields which are in all cases very low. The quantum yields of carbon monoxide and of carbon dioxide are about 0.005 and 0.009, respectively.

3. The presence of 1849 Å. radiation considerably increases the rate of formation of carbon monoxide but quantum yields at that wave length were not determined.

4. A polymer is produced whose exact nature is unknown but which shows the characteristic infrared carbonyl frequency of esters. The number of molecules of lactone which polymerize per quantum absorbed is much greater than the number which form carbon dioxide.

ROCHESTER, NEW YORK RECEIVED JANUARY 17, 1950

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[10] R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **72**, 101 (1950).

[11] *Cf.* G. Herzberg, "Infrared and Raman Spectra of the Polyatomic Molecules," D. Van Nostrand and Co., New York, N. Y., 1945, p. 388.