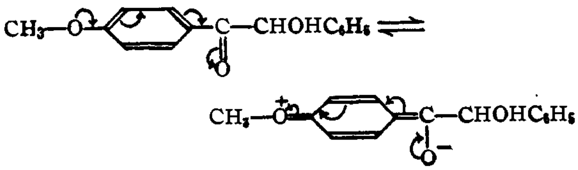
energy content) since it gives rise to benzanisoin and since there is the possibility for resonance between the CH_3O- group and the carbonyl in this molecule whereas anisbenzoin does not have this possibility



Experimental Part

Acetylation Products (IV) and (V).—Separate solutions of 5 0 g. each of anisbenzoin, benzanisoin, and anisoylphenylbromomethane in 25 cc. of acetic anhydride are refluxed gently with equal weights of freshly fused potassium acetate for thirty minutes. Each solution turns slightly yellow. After cooling they are worked up as described,[1] producing a cream-colored granular solid. Repeated fractional crystallizations from methyl alcohol yield in each case approximately 1.0 g. of the monoacetate, melting sharply at 83°, and 1.0 g. of the diacetate, melting at 127°.

Anal. Calcd. for $C_{17}H_{16}O_4$: $-OCH_3$, 10.9. Found: 11.2. Calcd. for $C_{19}H_{18}O_5$: $-OCH_3$, 9.5. Found: 9.7.

Both the mono and the diacetate on dissolving in alcohol and on gentle refluxing with concd. hydrochloric acid hydrolyze completely in thirty minutes to benzanisoin, melting and mix melting sharply with an authentic sample at 106°. The odor of ethyl acetate is observed.

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RECEIVED NOVEMBER 14, 1940

The Photolysis of the Aliphatic Aldehydes. IX. Glyoxal and Acetaldehyde

BY F. E. BLACET AND ROBERT W. MOULTON

A study of vapor phase mixtures of glyoxal and acetaldehyde has been made in an attempt to throw light on the primary photochemical process for glyoxal, as well as on the reaction

$$CH_3CHO + HCO \longrightarrow H_2 + CO + CH_3CO \quad (1)$$

which has been postulated as a part of the mechanism of acetaldehyde decomposition.[1]

Experimental Method

The photochemical technique was very similar to that previously described.[2] In a number of experiments glyoxal was mixed with carbon dioxide instead of with acetaldehyde. λ 3660 Å. was the principal radiation employed, since it is absorbed by glyoxal but not by acetaldehyde. The gaseous products were analyzed by well-known micro methods. Glyoxal was prepared by oxidizing ethylene with selenium dioxide in the presence of phosphorus pentoxide in a manner similar to that described by Riley and Friend.[3]

Experimental Results

Experiments with pure glyoxal gave a gaseous product which consisted of 97% CO and 3% H_2. This is in very good agreement with 97% CO, 2.5% H_2 and 0.5% unsaturated compounds reported by Norrish and Griffiths.[4] No unsaturated hydrocarbons were detected in our work. The percentages of carbon monoxide reported in the accompanying tables are based upon the sum of the two gases found, hence the per cent. of hydrogen in each case is the difference between 100 and the figure given for carbon monoxide.

Table I gives the percentages of carbon monoxide obtained in the photolysis of a series of glyoxal and acetaldehyde mixtures in which the ratio of these two substances was varied. Since it was evident that some polymerization was taking place during the runs, the reporting of ratios and percentages beyond two significant figures would not be justified.

Table II gives the results of a similar study in which carbon dioxide was substituted for acetaldehyde. In Fig. 1 the carbon monoxide to hy-

TABLE I

DATA OBTAINED FROM GLYOXAL–ACETALDEHYDE MIXTURES

Pressure, mm. $(CHO)_2$	CH_3CHO	$CH_3CHO/(CHO)_2$	% CO	Ratio CO/H_2
75	0	0	97	32
64	210	3.3	90	9.0
60	600	10	73	2.7
36	440	12	66	2.0
50	650	14	79	3.8
45	705	16	88	7.3

TABLE II

DATA OBTAINED FROM GLYOXAL–CARBON DIOXIDE MIXTURES

Pressure, mm. $(CHO)_2$	CO_2	Ratio $CO_2/(CHO)_2$	% CO	Ratio CO/H_2
75	0	0	97	32
100	216	2.2	89	8.1
75	465	6.2	79	3.8
56	555	10	66	2.0
40	510	13	77	3.3
50	685	14	86	6.1
40	555	14	90	9.0
40	630	16	90	9.0

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[1] (a) Blacet and Volman, THIS JOURNAL, **60**, 1243 (1938). (b) Leighton, *J. Phys. Chem.*, **42**, 749 (1938). (c) Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[2] Blacet and Taurog, THIS JOURNAL, **61**, 3024 (1939).

[3] Riley and Friend, *J. Chem. Soc.*, 2342 (1932).

[4] Norrish and Griffiths, *ibid.*, 2829 (1928).

drogen ratios are plotted against the respective ratios of acetaldehyde and carbon dioxide with glyoxal.

Although many tests were made, no methane was found in the photolysis products of glyoxal and acetaldehyde mixtures.

A small amount of exploratory work was done at shorter wave lengths as shown in Table III, where is given the percentage of carbon monoxide obtained in the photolysis of pure glyoxal at λ 3660, 3130 and 2537.

TABLE III

PER CENT. CARBON MONOXIDE OBTAINED AT DIFFERENT WAVE LENGTHS

λ, Å.	Glyoxal pressure, mm.	CO, %
3660	75	97
3130	90	93
2537	85	88

Discussion of Results

The absorption by glyoxal at λ 3660 is of the predissociation type[5] and some form of dissociation, although not required, is to be expected. A consideration of the energetics involved leads to the conclusion that a primary dissociation into two formyl radicals

$$\mathrm{CHOCHO} + h\nu \longrightarrow 2\mathrm{HCO} \qquad (2)$$

probably would not occur at this wave length. This is substantiated by electron diffraction measurements which have shown that resonance in the conjugated system has shortened the C–C bond distance in glyoxal.[6] The absence of methane from the gases formed in the photolysis of glyoxal-acetaldehyde mixtures is additional evidence that formyl is not a primary product, since otherwise reaction 1, followed by methane producing reactions,[1] would be expected to occur under some of the experimental conditions employed. Methane formation would have been evidence of both reactions 1 and 2.

Norrish and Griffiths[4] have suggested that in the primary process activated molecules are formed which dissociate according to the equations

$$\mathrm{CHOCHO'} + \mathrm{CHOCHO} \longrightarrow \mathrm{CO} + \mathrm{C_3H_4O_3} \qquad (3)$$

$$\mathrm{CHOCHO'} \longrightarrow 2\mathrm{CO} + \mathrm{H_2} \qquad (4)$$

It is evident that glyoxal does not induce the decomposition of acetaldehyde and that in the glyoxal–acetaldehyde mixtures the acetaldehyde was acting merely as an inert gas. Since reaction 3 is bimolecular while reaction 4 is unimolecular, the presence of a foreign gas would be expected to hinder reaction 3 much more than 4, and a decrease in the percentage of carbon monoxide would be anticipated with an increase of the ratio of foreign gas to glyoxal. Such a decrease was first observed with an acetaldehyde–glyoxal mixture, but since it is conceivable that acetaldehyde might have contributed in some other way to this change in ratio, mixtures of glyoxal and carbon dioxide were studied also. As shown in Fig. 1, the effects of acetaldehyde and carbon dioxide on the carbon monoxide to hydrogen ratio are very similar if not identical within the limits of experimental error in determining the average glyoxal pressure during an exposure.

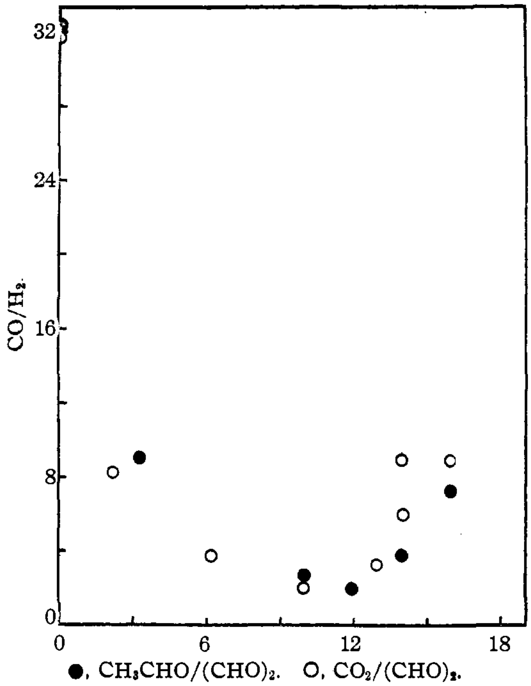

Fig. 1.—The carbon monoxide to hydrogen ratios plotted against the ratios of acetaldehyde and of carbon dioxide to glyoxal.

It was thought that by increasing the ratio of inert gas to glyoxal, reaction 4 could be made to predominate over 3 and the CO/H_2 ratio might be reduced to a value of 2 and would remain there with further increase of the first named ratio. Figure 1 shows a drop in CO/H_2 to a value of 2 at a foreign gas to glyoxal ratio of from 10 to 12, but contrary to expectations CO/H_2 does not remain constant beyond this point but rapidly increases again. This fact lends credence to reaction 4, but implies that some process other

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[5] Luthy, *Z. physik. Chem.*, **107**, 285 (1923).

[6] LuValle and Schomaker, THIS JOURNAL, **61**, 3520 (1939).

than reaction 3 must account for the high percentage of carbon monoxide found in experiments having a relatively high concentration of foreign gas. A reaction such as

$$\mathrm{CHOCHO'} \longrightarrow \mathrm{CO} + \mathrm{HCHO}$$

would meet the requirements but why it would predominate only at high pressures is not obvious. However, it is evident from the large variation of gaseous products that the primary process for glyoxal is the formation of an activated molecule which does not spontaneously dissociate into formyl radicals.

From the limited results obtained, it appears that the same chemical processes occur at λ 3660, 3130 and 2537, the variation being only one of degree.

DEPARTMENTS OF CHEMISTRY
STANFORD UNIVERSITY AND
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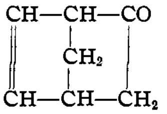
LOS ANGELES, CALIF.
RECEIVED OCTOBER 9, 1940

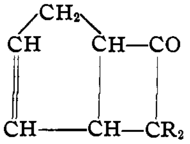
The Reaction of Cyclopentadiene and Ketene

BY BENJAMIN T. BROOKS AND GODFREY WILBERT

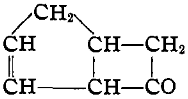
The now well-known Diels–Alder reaction was discovered by these authors[1] in a study of the reactions of cyclopentadiene with acrolein, acrylic acid and the anhydrides of maleic, citraconic and itaconic acids. All of these reactions give endomethylene products, acrolein giving endomethylene tetrahydrobenzaldehyde. It is obvious that ketene and cyclopentadiene would give an unsaturated ketone (1) which upon hydrogenation would give norcamphor, if the reaction follows the type Diels–Alder reaction. Norcamphor has been synthesized by Hinticka and Komppa[2] and by Diels and Alder[3] by other methods.

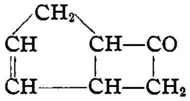
None of the ketenes appear to react with cyclopentadiene in the Diels–Alder fashion. Diphenylketene with cyclopentadiene gives a product (2) having the cyclobutanone structure[4,5] as originally suggested by Staudinger[6] and his co-workers. In view of these results, it appeared desirable to study the reaction of ketene itself upon cyclopentadiene.

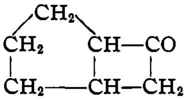

(1)


(2)

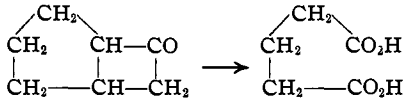
Recently Smith, Agre, Leekley and Prichard[5] were unable to obtain a reaction product of ketene and cyclopentadiene. We have found that ketene reacts with cyclopentadiene in a manner analogous to the reaction with diphenylketene, and not to give the product (1) to be expected from the Diels–Alder reaction. The resulting unsaturated ketone (3) or (4) was hydrogenated to the saturated ketone (5) which proved to be not identical with norcamphor.


(3)


(4)


(5)

The unsaturated ketones (3) and (4) obviously give the same hydrogenated product. That the saturated ketone (5) is not identical with norcamphor is indicative of this structure which was further confirmed by oxidation to glutaric acid.



All attempts to isolate the intermediate product cyclopentane-1,2-dicarboxylic acid were negative.

Experimental

Ketene.—This was prepared in the customary manner, passing acetone vapor rapidly through a 1/4" (6-mm.) copper tube maintained at about 700°. Unchanged acetone was condensed and the ketene absorbed from the gas stream by passing through toluene cooled to about −70° by solid carbon dioxide in isopropyl alcohol.

Cyclopentadiene.—This was prepared as needed by slowly distilling dicyclopentadiene through a packed four-foot (122-cm.) glass column, all of the product used distilling at 39–41°.

Reaction between Cyclopentadiene and Ketene.—Ketene was absorbed in two wash-bottles in series, each containing 300 g. of toluene, cooled as described. When the ketene dissolved in the toluene amounted to about 75 g., the toluene solutions were combined and 145 g. of freshly distilled cyclopentadiene were added and the solution placed in two small steel cylinders. The solution of ketene and cyclopentadiene in toluene was then heated under pressure at about 100° for one hour. The product was separated by fractional distillation, the material distilling at 150–160° being retained as the crude ketone. The crude unsaturated ketone, yield 78 g., a nearly colorless oil, thus obtained contained some cyclopentadiene

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(1) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(2) Hinticka and Komppa, *Chem. Zentr.*, **89**, II, 369 (1918).

(3) O. Diels and K. Alder, *Ann.*, **470**, 98 (1928).

(4) J. R. Lewis, G. R. Remage, J. L. Simonsen and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937).

(5) L. I. Smith, P. L. Agre, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 9 (1939).

(6) H. Staudinger, "Die Ketene," Stuttgart, p. 59, 1912; *Ann.*, **356**, 51 (1907).