[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. IX.[1] Acetylenic Aldehydes and Ketones

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The high moments of aldehydes and ketones are due primarily to the C=O group in the molecule. The high moments of these compounds have led certain authors[2] to the conclusion that the structure $R_2=C^+-O^-$ contributes appreciably to the molecule. This resonance requires that the more polar contributing form have six electrons in the valence shell of the carbon atom attached to the oxygen atom. When unsaturated groups are attached to the ketonic carbon atom this is no longer true and resonance takes place to a greater extent.

Preparation of Compounds.—The acetylenic aldehydes were obtained by treating the Grignard compound of the acetylenic hydrocarbon with ethyl orthoformate and subsequent hydrolysis of the diacetal according to a method devised by Moureu and Delange.[3] The acetylenic ketones were prepared from the corresponding Grignard reagents of the acetylenic hydrocarbon and acetic anhydride by a method used by Kroeger and Nieuwland.[4] Acetophenone and

TABLE I

PHYSICAL CONSTANTS OF ALDEHYDES AND KETONES

Compound	B. p., °C.		Mm.	d_{25}	$n^{25}D$
Benzaldehyde	64.5	65	12	1.0434	1.5428
Butylpropiolaldehyde	61.8	62.5	18	0.8770	1.4499
Amylpropiolaldehyde	77.5	78	17	.8712	1.4516
Phenylpropiolaldehyde	112.5	113	15	1.0556	1.5669
Acetophenone	94	94.5	20	1.0236	1.5322
Butylacetylacetylene	76	76.5	15	0.8631	1.4446
Amylacetylacetylene	89	89.5	15	.8616	1.4463
Phenylacetylacetylene	101	102	3	1.0239	1.5735

TABLE II

DIELECTRIC CONSTANTS AND DENSITITES OF SOLUTIONS OF ALDEHYDES AND KETONES

Solvent, benzene; temp. 25°

c_2	ϵ	d
	Benzaldehyde	
0.00000	2.2760	0.8738
.01273	2.4144	.8757
.01413	2.4312	.8769
.02445	2.5445	.8791
.04327	2.7533	.8833
	Butylpropiolaldehyde	
0.00000	2.2760	0.87360
.01417	2.4705	.87365
.01667	2.5092	.87366
.02719	2.6571	.87370
.03152	2.7081	.87374
	Amylpropiolaldehyde	
0.00000	2.2760	0.87358
.01203	2.4527	.87350
.01887	2.5404	.87345
.03808	2.8104	.87332
	Phenylpropiolaldehyde	
0.00000	2.2760	0.87358
.01704	2.5538	.87798
.02086	2.6166	.87888
.02705	2.7160	.88069
	Acetophenone	
0.00000	2.2760	0.87382
.01704	2.4606	.87758
.01940	2.4882	.87774
.01982	2.4901	.87810
	Butylacetylacetylene	
0.00000	2.2760	0.87350
.01554	2.4975	.87310
.02445	2.6078	.87288
.02520	2.6177	.87285
.04178	2.8237	.87244
	Amylacetylacetylene	
0.00000	2.2760	0.87282
.01916	2.5426	.87220
.02306	2.5910	.87214
.03257	2.7165	.87172
.05229	2.9650	.87120
	Phenylacetylacetylene	
0.00000	2.2760	0.87358
.01522	2.4980	.87721
.02924	2.6913	.88055
.03236	2.7393	.88129

TABLE III

POLARIZATIONS AND MOMENTS OF ALDEHYDES AND KETONES

Compound	P	MR_D	P_{A+M}	$\mu \times 10^{18}$
Benzaldehyde	190.3	32.03	158.3	2.77
Butylpropiolaldehyde	241.4	33.73	207.7	3.17
Amylpropiolaldehyde	248.4	38.40	210.0	3.18
Phenylpropiolaldehyde	275.4	42.27	233.1	3.36
Acetophenone	193.7	36.36	157.4	2.77
Butylacetylacetylene	250.2	38.23	212.0	3.20
Amylacetylacetylene	254.9	42.73	212.2	3.20
Phenylacetylacetylene	262.4	46.40	216.0	3.23

(1) Article VIII of this series, Koehl and Wenzke, THIS JOURNAL, **59**, 1418 (1937).

(2) Pauling and Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

(3) Moureu and Delange, *Compt. rend.*, **138**, 1339 (1904).

(4) Kroeger and Nieuwland, THIS JOURNAL, **58**, 1861 (1936).

TABLE IV

MOMENTS OF SOME ALDEHYDES AND KETONES

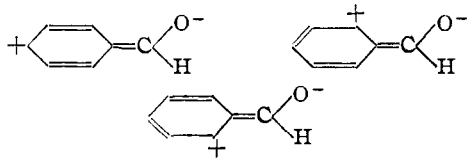
(Other investigators)

Butyraldehyde[5]	2.46×10^{-18}
Heptaldehyde[6]	2.56×10^{-18}
Benzaldehyde[7]	2.75×10^{-18}
Acetone[8]	2.72×10^{-18}
Diethyl ketone[9]	2.72×10^{-18}
Acetophenone[8]	2.94×10^{-18}

benzaldehyde were purchased from the Eastman Kodak Co. All compounds were purified by fractional distillation.

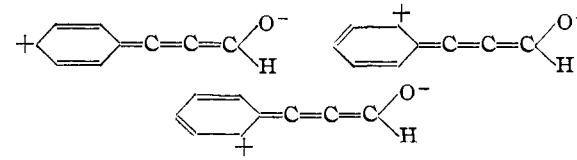
Discussion

As shown in the tables the moment of benzaldehyde is greater than that of either butyraldehyde or heptaldehyde. The higher moment of benzaldehyde is due to the greater contribution of the polar forms



The moment of acetophenone is slightly higher (using the value 2.77 obtained by the present authors) than that of the aliphatic ketones. In this case the contribution of the polar forms of the type referred to in benzaldehyde is in part offset by the steric repulsion of the methyl and phenyl groups. This repulsion results in a widening of the angle between those two groups and reduces the angle between the phenyl group and the ketonic oxygen. These changes in the angles partly offset the increase in moment due to the resonance produced by the phenyl group. The moments of the acetylenic aldehydes and ketones are much higher than those of either the alkyl or phenyl derivatives. This means that the forms

contribute heavily to the structure of the molecule. With phenylpropiolaldehyde and phenylacetylacetylene we have the additional resonance due to the phenyl radical giving in phenylpropiolaldehyde the structures



and analogous structures with phenylacetylacetylene. This results in the phenyl derivatives of the acetylenic aldehydes and ketones having slightly higher moments than the corresponding aliphatic derivatives.

Summary

1. Electric moments have been determined for a number of aldehydes: benzaldehyde, butylpropiolyl-, amypropiolyl- and phenylpropiolyl; and several ketones, acetophenone, butylacetylacetylene, amylacetylacetylene and phenylacetylacetylene.

2. The moments of the acetylenic aldehydes and ketones are considerably higher than those of the alkyl and phenyl derivatives. These higher moments have been explained by the contribution of highly polar structures in resonance with the classical form.

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(5) Hassel and Naeshagen, *Z. physik. Chem.*, **6B**, 152 (1929).
(6) Errera and Sherrill, THIS JOURNAL, **52**, 1993 (1930).
(7) Williams, *ibid.*, **50**, 2350 (1928).
(8) Hassel and Naeshagen, *Z. physik. Chem.*, **B4**, 217 (1929).
(9) Wolf and Lederle, *Physik. Z.*, **29**, 948 (1928).