of expressing the results serves to bring the experiments with the various esters to a common basis for comparison of polymerization rates. Each curve of Fig. 3 represents a single typical run. If we assume the chain mechanism described by Norrish and Smith[6] and applied by them to methyl methacrylate, the similarity of the shapes and position of the curves for phenyl, benzyl, and cyclohexyl methacrylate indicates that all the steps involved in these chain reactions have similar rate constants. Methyl and butyl esters have similar initial slopes, but the curve for the methyl ester has an earlier inflection time. This would indicate either that in the case of methyl compound the chain terminating step is more sensitive to viscosity change or that the viscosity increases more rapidly than in the case of the butyl compound, or possibly both factors are pertinent. It is believed that the present data are insufficient to warrant further speculation concerning the causes of such variations.

Summary

1. The heat of polymerization of several esters of methacrylic acid are compared using an improved isothermal calorimeter.

2. The $-\Delta H$ values obtained as kcal./mole are: methyl, 13.0; *n*-butyl, 13.5; cyclohexyl, 12.2; benzyl, 13.4; phenyl, 12.3. The average deviation was found to be about ±0.2.

3. These esters have generally similar $-\Delta H$ values, though the values for the cyclohexyl and phenyl esters are slightly the lower.

4. The rates of polymerization are similar for the esters having cyclic structures and greater than the rates for the alkyl esters.

ROCHESTER 4, N. Y. RECEIVED MARCH 7, 1946

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[6] Norrish and Smith, *Nature*, **150**, 336 (1942).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of Ketene and of Several Polar Molecules Containing Conjugated Systems

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

The striking results given by electron diffraction for the structure of ketene[1] made very desirable the measurement of the dipole moment of the molecule in order to obtain evidence of the contributions of the polar structures indicated by electron diffraction. The availability of samples of four aldehydes and nitriles and an ester with conjugated systems in their molecules made possible the extension of earlier work in this laboratory on similar molecules.[2]

Experimental Method

The dielectric constants of the vapors of these substances were measured with the apparatus and technique previously described,[3] and used to calculate the polarizations and dipole moments of the molecules.

Several of the substances showed a tendency to polymerize on the walls of the apparatus. As it was found that this could be largely prevented by warming the glass tubing, the whole vacuum system was wrapped with a coil of nichrome wire and electrically heated. Under these temperature conditions, the Apiezon stopcock grease ordinarily used had to be replaced by a special grease made of mannitol, dextrose and glycerol, which had a relatively high melting point.

Materials

Ketene.—The material was prepared by the pyrolysis of acetone, the vapor passing over the hot filament of the generator. A long reflux water condenser removed most of the acetone vapor, and all products condensing at −80° were collected. The ketene was purified by the method of Rice and his co-workers.[4] With the receiver at −80°, the condensate was warmed rapidly to 50°, a reflux water condenser being used. This was repeated twice with warming to 0° only. The fourth distillation was the same, but only the middle fraction was collected. This procedure, it was believed, would remove the last traces of dissolved ethylene from the ketene. The material was sealed on to the vacuum system of the dielectric cell in a side-arm and was measured by the two-point method, the ketene being maintained throughout the runs at about −50°, which was about 10° below its normal boiling point (−41°). Two samples of ketene were prepared and measured, the reproducibility of the moment obtained being taken as evidence of the purity of the substances used.

Acrolein, Methacrolein.—Pure samples given us by the Shell Development Company through the kindness of Dr. Otto Beeck were subjected only to the double distillation required to introduce the sample of vapor into the dielectric cell.

Ethyl Sorbate.—Material kindly furnished by the Carbide and Carbon Chemicals Corporation, containing possibly 0.2% sorbic acid, was subjected only to the double distillation required to introduce it into the cell.

Methacrylonitrile.—Material kindly furnished by the United States Rubber Company General Laboratories was believed to be quite pure but was fractionated to remove the hydroquinone inhibitor and any possible traces of polymer, the fraction boiling in the range 88.9-89.4° being used.

4-Cyanobutadiene-1,3.—A sample kindly given us by the du Pont Company contained 0.1% catechol as a stabilizer, which was removed in the usual double distillation carried out in the vacuum system.

Experimental Results

The results of individual runs at each absolute temperature, T, are given in Table I for the molar

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[1] Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[2] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

[3] McAlpine and Smyth, *ibid.*, **55**, 453 (1933); deBruyne and Smyth, *ibid.*, **57**, 1203 (1935); Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1943).

[4] Rice, Greenberg, Waters and Vollrath, *ibid.*, **56**, 1760 (1934).

polarization, P, of all the substances. The dipole moment, μ, was calculated from the equation, $\mu = 1.28 \times 10^{-20}[(P - MR_D)T]^{1/2}$ in which the molar refraction, MR_D, was obtained or calculated from the literature. Where several values are given at one temperature in Table I, it signifies that the measurements were made by the "two-point" method, in which the cell capacity was measured at only two pressures, while, otherwise, several measurements were made over a wide range of pressure. The average moment value for each substance and the value of the molar refraction used in calculating it are given in Table II.

TABLE I

POLARIZATIONS AND DIPOLE MOMENTS

T, °K.	P	$\mu(\times 10^{18})$	T, °K.	P	$\mu(\times 10)^{18}$
Ketene			440.9	118.4	2.65
Sample No. 1			465.6	110.3	2.64
397.8	43.03	1.45		112.1	2.67
	44.22	1.47	Ethyl Sorbate		
	44.15	1.47	506.9	94.86	2.07
Sample No. 2				94.48	2.07
429.0	38.98	1.41		95.04	2.08
	38.98	1.41		93.43	2.05
	40.84	1.45	4-Cyanobutadiene-1,3		
	41.65	1.47	426.7	240.9	3.88
444.7	39.83	1.45	438.0	239.8	3.92
	39.33	1.44		240.4	3.93
446.3	39.81	1.46		239.4	3.92
	39.81	1.46		234.6	3.88
	39.14	1.44		241.8	3.93
Acrolein				240.4	3.93
377.0	162.8	3.02	463.7	223.5	3.88
	165.2	3.04		221.1	3.86
396.3	158.5	3.05	Methacrylonitrile		
426.7	146.7	3.03	394.9	228.5	3.68
458.6	136.9	3.02	410.9	221.4	3.69
478.1	135.4	3.06	428.4	215.3	3.71
Methacrolein			456.2	201.0	3.68
366.0	141.0	2.69		201.0	3.68
397.8	136.9	2.75	472.8	196.1	3.70
412.5	126.7	2.67		196.1	3.70

TABLE II

MOLAR REFRACTION AND DIPOLE MOMENT VALUES

	MR_D	$\mu(\times 10^{18})$
Ketene	11.0[a]	1.45
Acrolein	16.14[a]	3.04
Methacrolein	21.0[b]	2.68
Ethyl sorbate	23.27[c]	2.07
4-Cyanobutadiene-1,3	26.36[d]	3.90
Methacrylonitrile	20.2[e]	3.69

[a] Taken or calculated from refractions in Landolt-Börnstein (5th edition). [b] Hearne, Tamele and Converse, *Ind. Eng. Chem.*, **33**, 805 (1941). [c] Auwers and Eisenlohr, *J. prakt. Chem.*, (2) **84**, 92 (1911). [d] Coffman, THIS JOURNAL, **57**, 1981 (1935). [e] Calculated by adding 4.6, the refraction of a CH_2 group, to the refraction measured for acrylonitrile by Hurdis and Smyth.[2]

Discussion of Results

The moment of ketene, 1.45, is much lower than the value to be expected on the basis of the two structures generally written as contributing to the structures of aldehydes and ketones:[2] $CH_2{=}C{=}O$ I and $CH_2{=}C^+{—}O{:}^-$ II. In addition, one might write three less stable structures, $C^+H_2{—}\ddot{C}{—}O{:}^-$ III, and two, such as $H^+\ddot{C}H{—}\ddot{C}{—}O{:}^-$ IV. The possible small contributions from these structures would raise the moment value. The reason for carrying out these somewhat difficult measurements on ketene was that electron diffraction[1] indicated a shortening of 0.07 Å. in the carbon–oxygen distance below that of the carbon–oxygen double bond, which was accounted for by supposing a 25% contribution from the structure $\bar{:}CH_2{—}C{\equiv}O^+$ V. If it is assumed that structures I and II contribute the remaining 75% with the non-polar I contributing 0.53 and the polar 0.47 of the 75%, that is, analogous to the approximately equal contributions found in acetone,[5] the resultant moment of the molecule is calculated from the standard bond lengths and the electronic charge to be $3.17 - 2.04 = 1.13$ with the positive end of the dipole toward the oxygen. Contributions from structures III and IV would lower this resultant moment, and, if large enough, would reverse its direction. One can write additional structures such as $H^+CH{\equiv}C{—}O\bar{:}$ VI, which tend to put the negative end of the resultant dipole toward the oxygen. Although the shortening of the carbon–carbon bond by contributions from VI would be decreased by contributions from III and IV, the absence of measurable departure of the carbon–carbon bond length from that of the normal double bond shows that contributions from structures such as VI must be very small, since shortening due to triple bond structure would tend to outweigh lengthening by equivalent contributions from single bond structures.

With structures III and IV neglected, approximate equations have been set up by the method of Pauling[5] for the interatomic distances in terms of the force constants, the standard bond lengths, and the fractional contributions, 0.53 x, 0.47 x, y and z, from the different structures, a 53/47 ratio being assumed for I and II. Solution of these equations together with one for the resultant moment in terms of the moments calculated for the different structures and the fractional contributions of the structures could not be obtained for a dipole with its negative charge toward the oxygen. However, with the positive end of the dipole toward the oxygen, good agreement could be obtained between the observed and the calculated values of the bond lengths and the moment with the following percentage contributions from the different structures: I, 37%;

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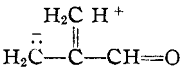
(5) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

II, 32%; V, 29%; VI, 2%. If this calculation were correct, the oxygen atom would have only a very small negative charge, while the carbon to which it is linked would have a considerable positive charge and the other carbon a negative charge equal to the absolute difference between the other two charges. The assumptions underlying these calculations as well as the small experimental differences in bond length are so approximate that the apparent indication of a reversal of the expected direction of the molecular moment cannot be regarded as established. Such a distribution of charge would be somewhat analogous to that in carbon monoxide, where the contributions of the two polar structures of the three probable structures, $C{=}O$, $^{+}C{-}O{:}^{-}$, and $^{-}C{\equiv}O^{+}$, must be approximately equal, since the moment is practically zero. The measurements of electron diffraction and dipole moment agree in showing much less negative charge on the oxygen of ketene than is found in the aldehydes and ketones. The large positive charge on the one carbon and the negative on the other are consistent with the chemical behavior of ketene,[6] which qualitatively requires such a charge distribution but does not require the end carbon to have a larger negative charge than the oxygen. However, the considerable difference indicated between the charge distribution in the carbonyl group of ketene and that in the carbonyl of aldehydes and ketones is consistent with the differences in chemical behavior.

From the moment value of acrolein in benzene solution,[7] 2.88, it was estimated[2] that the value in the vapor state should be close to 3.11. The value 3.04 in Table II justifies this estimate and the polar structures proposed[2] to explain the increase of moment of acrolein over that of propionaldehyde. The moment found for *trans*-crotonaldehyde, 3.67, is 0.63 higher than that of acrolein, a fact which was explained[2] in terms of hyperconjugation and the transmission of charge shift through the conjugated system from the methyl group to the oxygen. In methacrolein, which, according to Table II, has a moment, 2.68, lower by 0.36 than that of acrolein, the charge shift from the methyl group opposes instead of reënforcing the polarity due to the carbonyl group. These relations are illustrated by the following typical polar structures

Propionaldehyde	$(CH_3)H^{+}CH{=}CH{-}\overset{-}{O}{:}$
Acrolein	$H^{+}\ddot{C}H{-}CH{=}CH{-}\overset{-}{O}{:}$
Crotonaldehyde	$H^{+}CH_2{=}CH{-}CH{=}CH{-}\overset{-}{O}{:}$
Methacrolein	$H^{+}\ddot{C}H{-}C(CH_3){=}CH{-}\overset{-}{O}{:}$ and  $H_2\overset{-}{\ddot{C}}{-}\overset{H_2C\;H^{+}}{\overset{\Vert}{C}}{-}CH{=}O$

The second of the two typical structures for methacrolein should have the same moment as the polar structure written for propylene, $H^{+}CH_2{=}CH{-}\overset{-}{\ddot{C}}H_2$. If the three possible structures of this type made the same contribution to the structure of the molecule as do the three for propylene, a moment equal to that of propylene, 0.35, would so nearly oppose the carbonyl moment as to reduce it by about 0.33 unit, provided that the methyl group were in the *cis* position relative to the oxygen. Calculation shows that, in this position, induction between the carbonyl dipole and the methyl group should give a moment lowering of about 0.24. As the *cis* position is an extreme one, the actual moment lowering below that of acrolein should be less than the sum of these two effects and close to the observed 0.36.

One might regard the dipole moment of ethyl sorbate, $CH_3{-}CH{=}CH{-}CH{=}CH{-}COOC_2H_5$, I, as the resultant of the moment of a dipole like that in ethyl acetate,[8] 1.76, and the moment of 1-methylbutadiene,[9] 0.68. The solution moments[10] of ethyl acetate, ethyl propionate, ethyl butyrate, and ethyl palmitate and ethyl stearate, which lie between 1.81 and 1.88, show little or no change in moment with increase in the length of the carbon chain. It is reasonable, therefore, to attribute the difference between the vapor moments of ethyl acetate and ethyl sorbate, 0.31, to the conjugated system in the latter molecule. Polarity like that in 1-methylbutadiene would result in contributions from three structures such as $H^{+}CH_2{=}CH{-}CH{=}CH{-}\overset{-}{\ddot{C}}H{-}COOC_2H_5$, II. If it is assumed that the $-COOC_2H_5$ group moment makes its usual angle 70° with the bond of the group to the rest of the molecule, while the moment of the rest of the molecule acts in the direction of this bond, the calculated resultant moment, 2.08, is indistinguishable from the observed value, 2.07. One would, however, expect that the shift of charge in the above polar structure would extend to the oxygen, as in the aldehydes with conjugated systems, giving three structures such as $H^{+}CH_2{=}CH{-}CH{=}CH{-}CH{=}C{-}\overset{-}{\ddot{O}}(OC_2H_5)$ III. The large rise in moment[2] from acrolein to *trans*-crotonaldehyde, 0.63, is practically identical with the rise from acrylonitrile to *trans*-crotononitrile, 0.62, and with the moment of 1-methylbutadiene, 0.68, presumably, because of an equivalent charge shift through a five-atom chain in each case. The longer charge shift in structure III above should, if the chain is extended as assumed in the calculation, tend to give a greater increase in moment than that of the

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[6] Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 663, 1913; Müller, "Neuere anschauungen der organischen Chemie," J. Springer, Berlin, 1940 (Edwards Brothers, Inc., Ann Arbor, Mich., 1944), p. 154.

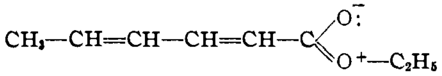
[7] Coomber and Partington, *J. Chem. Soc.*, 1444 (1938).

[8] Zahn, *Physik. Z.*, **33**, 730 (1932).

[9] Hannay and Smyth, THIS JOURNAL, **65**, 1931 (1943).

[10] Smyth and Walls, *ibid.*, **53**, 527 (1931); Wolf and Gross, *Z. physik. Chem.*, **B14**, 305 (1931); Lewis and Smyth, THIS JOURNAL, **62**, 1529 (1940).

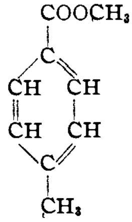
shorter chains. However, the large contribution from the structure



$$CH_3—CH=CH—CH=CH—C{\overset{\textstyle O\bar{:}}{\underset{\textstyle O^{+}—C_2H_5}{}}}$$ IV

the moment of which is included in the acetate moment, 1.76, would greatly reduce the contribution from structure III and thus lessen the increase in moment due to it. Another factor may be that the long chain is not completely extended so that the charge separation is no greater than in the shorter chains. In spite of the number of factors involved, it may be concluded that the moment of the molecule may be accounted for by structures II and IV, while the contribution of structure III must be much smaller than that of analogous structures in aldehydes.

It is of interest to note that methyl *p*-toluate contains, essentially, the chain constituting ethyl sorbate.

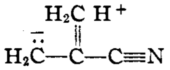


The moment of methyl benzoate is 1.91,[11] while that of methyl *p*-toluate is 2.12,[11] showing a rise of 0.21 comparable to the rise of 0.31 in the moment of ethyl sorbate over that of ethyl acetate.

It has been shown previously[2] that acrylonitrile has a moment, 3.88, slightly lower than that of propionitrile, 4.00, a lowering attributed to the contribution from a structure with positive nitrogen and negative terminal carbon, which opposed the contributions from structures with positive charge on the terminal carbon or its hydrogens. The same approximate compensation of the polarities due to contributions from such structures is apparent in the moment, 3.90, of the longer molecule of 4-cyanobutadiene-1,3, which is practically indistinguishable from that of acrylonitrile. Here, the contributions of structures such as $^{+}CH_2—CH=CH—CH=C=\bar{N}:$ and $H^{+}\ddot{C}H—CH=CH—CH=C=\bar{N}:$ are opposed by the contribution of $:\bar{C}H_2—CH=CH—CH=C=N^{+}$, so that the increase in the length of the chain over that of acrylonitrile does not increase the moment.

The moment of methacrylonitrile, 3.69, shows a drop of 0.19 or 5% from that of acrylonitrile, analogous to the drop of 0.36 or 12% from the moment of acrolein to that of methacrolein. One can write for methacrylonitrile structures analogous to those of methacrolein:

$$H^{+}\ddot{C}H—C(CH_3)=C=\bar{N}:$$ and



$$H_2\bar{\ddot{C}}—\overset{\textstyle H_2C\ H^{+}}{\overset{\|}{C}}—C\equiv N$$

The propylene moment in the second structure makes such an angle with the cyanide moment that it should have no observable effect on the resultant moment of the molecule and the inductive effect between the methyl group and the cyanide should be small. One would thus expect the methyl group to have less effect in the nitrile than in the aldehyde, as observed, but the effect would be expected to be still smaller than the observed.

Summary

The dielectric constants of the vapors of ketene, acrolein, methacrolein, ethyl sorbate, 4-cyanobutadiene-1,3 and methacrylonitrile have been measured over a range of temperature and pressure and used to calculate the dipole moments of the molecules.

The low dipole moment of ketene is consistent with the results of electron diffraction and indicates some analogy between its structure and that of carbon monoxide. The oxygen has much less negative charge than the ordinary carbonyl oxygen. The moments of the four molecules with conjugated systems give evidence of resonating structures and consequent polarities analogous to those previously observed in this laboratory.

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(11) Donle, *Z. physik. Chem.*, **B14**, 326 (1931).