[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Magnetic Susceptibilities of Some Methyl Derivatives of Methane and Ethylene[1]

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The diamagnetic susceptibilities of several compounds have been measured: propane, isobutane, neopentane, propylene, *cis*- and *trans*-butene-2, isobutene and tetramethylethylene. The Quincke method was used. The experimental molar susceptibilities deviate from a simple additivity rule. The standard heats of formation of the methyl derivatives of methane and of ethylene show the same types of deviation from this rule as do the corresponding molar susceptibilities. The experimental data for the methyl derivatives of methane may be satisfactorily interpreted when tetrahedral interactions are assumed. In case of the methyl derivatives of ethylene, the deviations may be simply related to the geometry of the ethylenic rectangle.

The molar diamagnetic susceptibilities of the halogen derivatives of methane deviate considerably from a simple additivity rule. We showed recently[2] that these susceptibilities may be interpreted successfully as being equal to the sum of atomic increments plus six interaction terms corresponding to the edges of a tetrahedron. The electron clouds of the halogen atoms are sufficiently large so that a mutual crushing takes place. This will reduce the molar susceptibility of the molecule since atomic susceptibilities are, to a first approximation, proportional to the square of the radii of the electron orbits. This is supported by the facts that the magnitude of the halogen–halogen interaction increases with increasing size of the halogen atom and that hydrogen–halogen interactions are small except for fluorine.

Mutual crushing of the electron clouds should give rise to repulsive potentials. These potentials should manifest themselves in the standard heats of formation of the compounds involved. Unfortunately, reliable thermochemical data for the halogen derivatives of methane and ethylene are not yet available. The standard heats of formation of the methyl derivatives are known from the work of Rossini and co-workers.[3] The molar susceptibilities of some of these compounds have been measured and are reported in this paper.

Experimental

The magnetic susceptibilities of these compounds have been measured: propane, isobutane, neopentane, propylene, *cis*- and *trans*-butene-2, isobutene and tetramethylethylene. All measurements were made by means of the Quincke method,[4] using an apparatus previously described.[5] Carefully purified benzene ($\chi_g = -0.702 \times 10^{-6}$) was employed as a standard for the measurements. Since all but one of the hydrocarbons are vapors at room temperatures, a high pressure Quincke tube was used.

All of the hydrocarbons except *trans*-butene-2 and tetramethylethylene were pure grade as supplied by the Phillips Petroleum Company and were used without further purification. The *trans*-butene was obtained by distillation of a mixture of the *cis*- and *trans*-isomers in a Hyper-Cal Podbielniak column. The infrared spectra of the *trans*-compound so obtained showed no absorption due to the *cis*-isomer.[6] The tetramethylethylene was obtained on loan from API Research Project 45 through the courtesy of Professor Boord, Department of Chemistry, Ohio State University. Its purity was greater than 99% and the compound was free of peroxides. The experimental results are summarized in Table I. The second column in this table gives the measured molar susceptibility and the fourth column the calculated susceptibility. The method used to make these calculations will be described later. The third and last columns give the change in susceptibility which result when a hydrogen atom is replaced by a methyl group. It is believed that our experimental data are reliable to 1%. Bitter's[7] values for methane, ethane and ethylene are also included in the table. Their critical temperatures are such that they could not be studied in our present apparatus. The value of 12.0 for ethylene seems to us to be much too low. Bitter has also reported 40.5 and 56.3 for the molar susceptibility for propane and isobutane, respectively. Pascal[8] reported the molar susceptibility for trimethylethylene.

TABLE I

MOLAR DIAMAGNETIC SUSCEPTIBILITIES

Compound	$-\chi_{\text{expt.}} \times 10^6$	Δ	$-\chi_{\text{calcd.}} \times 10^{+6}$	Δ
A. Methyl derivatives of methane				
CH_4	12.2[7]		13.4	
		15.1		13.4
CH_3CH_3	27.3[7]		26.8	
		12.3		12.8
$CH_2(CH_3)_2$	39.6		39.6	
		12.1		12.1
$CH(CH_3)_3$	51.7		51.7	
		11.4		11.4
$C(CH_3)_4$	63.1		63.1	
B. Methyl derivatives of ethylene				
$CH_2{=}CH_2$[7]	12.0		20.4	
		19.5		11.4
$CH_2{=}CHCH_3$	31.5		31.8	
		11.8		11.4
$CHCH_3{=}CHCH_3$ *trans*	43.3		43.2	
		11.1		10.5
$CHCH_3{=}CHCH_3$ *cis*	42.6		42.3	
		12.9		12.3
$CH_2{=}C(CH_3)_2$	44.4		44.1	
		10.3		10.5
$CHCH_3{=}C(CH_3)_2$[8]	54.7		54.6	
		11.2		11.3
$C(CH_3)_2{=}C(CH_3)_2$	65.9		65.9	

Discussion

It is interesting to compare the molar susceptibilities of the methyl derivatives of methane and ethylene with their standard heats of formation. The necessary data are from Rossini and co-workers.[3] The following information was used to calculate the heats of formation at 0°K. from C(gas), H(g) and the methyl radical:

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 103.24 \text{ kcal.}$$

$$C(\text{graph}) \longrightarrow C(g) \qquad \Delta H = 169.74 \text{ kcal.}^9$$

$$CH_4 \longrightarrow CH_3 + H \qquad \Delta H = 100.8 \text{ kcal.}^{10}$$

It follows that

$$C(\text{gas}) + 3H(g) \longrightarrow CH_3 \qquad \Delta H = -291.44 \text{ kcal.}$$

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[1] Presented before the Division of Inorganic and Physical Chemistry, 118th Meeting of the American Chemical Society, Chicago, Sept. 3–8, 1950. This work was supported by Contract N6-onr-231, Task Order 6, with the Office of Naval Research, United States Navy.

[2] J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **72**, 333 (1950).

[3] American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties Series III, Vol. I.

[4] G. Quincke, *Ann. Physik*, **24**, 247 (1885); **34**, 401 (1888).

[5] J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **71**, 1797 (1949).

[6] D. E. Campion, Ph.D. Thesis, 1949, University of Colorado.

[7] F. Bitter, *Phys. Rev.*, **33**, 389 (1927).

[8] "International Critical Tables," Vol. 6, McGraw-Hill Book Company, Inc., New York, N. Y., p. 192.

[9] L. Gerö, *J. Chem. Phys.*, **16**, 1011 (1948).

[10] G. B. Kistiakowsky and E. R. Van Artsdalen, *ibid.*, **12**, 469 (1944).

The results of the calculations are given in Table II.

TABLE II

MOLAR HEATS OF FORMATION

Compound	$-\Delta H_{\text{expt.}}$ kcal.	$-\Delta$	$-\Delta H_{\text{calcd.}}$ kcal.	$-\Delta$
A. Methyl derivatives of methane				
CH_4	392.20	17.94	392.20	17.70
CH_3CH_3	374.26	15.50	374.42	15.63
$CH_2(CH_3)_2$	358.76	13.34	358.79	13.56
$CH(CH_3)_3$	345.42	11.77	345.23	11.49
$C(CH_3)_4$	333.65		333.74	
B. Methyl derivatives of ethylene				
$CH_2{=}CH_2$	531.43	12.42	531.40	12.33
$CH_2{=}CHCH_3$	519.01	12.50	519.07	12.32
$CHCH_3{=}CHCH_3$ *trans*	506.51	13.69	506.75	13.79
$CHCH_3{=}CHCH_3$ *cis*	505.32	11.67	505.28	11.72
$CH_2{=}C(CH_3)_2$	507.34	13.12	507.35	13.79
$CH(CH_3){=}C(CH_3)_2$	494.22	14.18	493.56	13.20
$C(CH_3)_2{=}C(CH_3)_2$	480.04		480.36	

One notes that when H– atom in CH_4 is replaced by a methyl group, the heat of formation changes by 17.94 kcal. This change decreases as the compound becomes more highly methylated and becomes 11.77 kcal. when the H– atom in isobutane is replaced. As may be seen from Table IA, a similar situation obtains for the molar susceptibilities. It is apparent that the molar susceptibilities and the heats of formation of these compounds both deviate from the additivity rule in the same manner. These molar quantities may be interpreted empirically if it is assumed that they consist of contributions from C, H, CH_3 and six interaction terms corresponding to the edges of a tetrahedron. For example, the susceptibility for isobutane may be written as

$$\chi = C + H + 3CH_3 + C(H\text{-}CH_3) + 3(CH_3\text{-}CH_3) \quad (1)$$

For purposes of calculation it is convenient to rearrange equation (1) into the equivalent form

$$\begin{aligned} &= 3[1/4C + CH_3 + 3/2(CH_3\text{-}CH_3)] \\ &\quad + [1/4C + H + 3/2(H\text{-}H)] \\ &\quad + 3[(N\text{-}CH_3) - 1/2(H\text{-}H) - 1/2(CH_3\text{-}CH_3)] \quad (2) \end{aligned}$$

It is apparent that there are two classes of groups. The first is of the type $[1/4C + CH_3 + 3/2(CH_3\text{-}CH_3)]$ or $[1/4C + H + 3/2(H\text{-}H)]$ and involves atomic increments and interactions between like groups. The second is $[(H\text{-}CH_3) - 1/2(H\text{-}H) - 1/2(CH_3\text{-}CH_3)]$ and involves mixed interactions. Thus there are three adjustable constants which is the minimum number possible. We have used our experimental data on the molar susceptibilities to calculate them and the results are given in Table III. Similar equations were set up for the heats of formation. The bond and interaction energies calculated from all the experimental data by the methods of least squares are also given in Table III. The data in this table may be used to calculate the molar susceptibilities and heats of formation of the compounds involved. The results are given in Tables IA and IIA, column four. The agreement with the experimental values is excellent and shows that the deviations from an additivity rule are simply related to the geometry of a tetrahedron. Urey and Bradley[11] and Heath and Linnett[12] found that a similar situation occurred with force constants for tetrahedral molecules. It was necessary to assume the existence of repulsive forces between non-bonded atoms in a manner similar to that which is done here.

TABLE III

METHYL DERIVATIVES OF METHANE

A. Group and interaction susceptibilities	$-\chi \times 10^{+6}$
$1/4C + H + 3/2(H\text{-}H)$	3.36
$1/4C + CH_3 + 3/2(CH_3\text{-}CH_3)$	15.79
$(H\text{-}CH_3) - 1/2(H\text{-}H) - 1/2(CH_3\text{-}CH_3)$	0.32
B. Bond and interaction energies	ΔH, kcal.
$C\text{-}H + 3/2(H{\cdot}H)$	−98.03
$C\text{-}CH_3 + 3/2(CH_3{\cdot}CH_3)$	−83.43
$(H{\cdot}CH_3) - 1/2(H{\cdot}H) - 1/2(CH_3{\cdot}CH_3)$	1.04

If one uses the calculated values for the atomic susceptibilities given previously,[2] the absolute values for the interaction increments may be estimated. The present experimental data give +0.1 × 10^6 for the (H–H) interaction; it is quite small and in reasonable agreement with the value of +0.2 × 10^6 previously given. The (CH_3–CH_3) and (H–CH_3) interactions are −0.37 × 10^6 and −0.46 × 10^6, respectively. They are negative and thus make a diamagnetic contribution to the susceptibility. This contrasts with the halogen–halogen[2] interactions where a paramagnetic contribution occurs whose magnitude increases with increasing size of the halogen atom. The reason for the difference is not clear. However, it may be due to the presence of three protons in the electron cloud of the methyl group and the resulting problem involving restricted rotation about the C–C bond.

An examination of the data presented in Tables IB and IIB shows that the molar susceptibilities and heats of formation of the methyl derivatives of ethylene do not show large deviations from an additivity rule. However, small deviations do occur. One notes that the molar susceptibility and heat of formation for *trans*-butene-2 are greater than those for the *cis*-compound; and isobutene shows larger values than either of the other isomers. Simple ethylenic compounds have a planar structure. The molar properties listed in Tables IB and IIB were examined to see if they could be related to the geometry of the ethylenic rectangle. Interactions between non-bonded atoms or groups are assumed to take place along the edges of this rectangle.

The empirical equations used to represent the molar diamagnetism of the ethylenes will be illustrated by taking $CH_2{=}CHCH_3$ as an example. The molar susceptibility is written as

$$\chi = C{=}C + 3H + CH_3 + CH_3{\cdot}H + H{\cdot}H + H{:}H + CH_3{:}H \quad (3)$$

Here C=C represents the susceptibility due to two carbon atoms and the double bond, H and CH_3 the susceptibility due to hydrogen and a methyl group,

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[11] Urey and Bradley, *Phys. Rev.*, **38**, 1969 (1931).

[12] D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 561 (1948).

$CH_3{\cdot}H$ and $H{\cdot}H$ represent interactions between non-bonded groups along the edges of the ethylenic rectangle which are perpendicular to the double bond, and $H{:}H$ and $CH_3{:}H$ those interactions between non-bonded groups along the edges of the rectangle which are parallel to the double bond. For purposes of calculation it is convenient to rearrange equation (3) into an equivalent form which is

$$\begin{aligned}\chi = {} & 3[1/4C{=}C + H + 1/2H{\cdot}H + 1/2H{:}H] \\ & + [1/4C{=}C + CH_3 + 1/2CH_3{\cdot}CH_3 + 1/2CH_3{:}CH_3] \\ & + [CH_3{\cdot}H - 1/2CH_3{\cdot}CH_3 - 1/2H{\cdot}H] \\ & + [CH_3{:}H - 1/2CH_3{:}CH_3 - 1/2H{:}H]\end{aligned} \qquad (4)$$

The equation again contains two classes of groups. However, we now have four adjustable constants owing to the fact that two edges of the ethylenic rectangle are different. The values for these groups which were calculated by the methods of least squares from the experimental data in Table IB are listed in Table IVA.

TABLE IV

METHYL DERIVATIVES OF ETHYLENE

A. Group and interaction susceptibilities

	$-\chi \times 10^6$
$1/4C{=}C + H + 1/2H{\cdot}H + 1/2H{:}H$	5.10
$1/4C{=}C + CH_3 + 1/2CH_3{\cdot}CH_3 + 1/2CH_3{:}CH_3$	16.47
$H{\cdot}CH_3 - 1/2H{\cdot}H - 1/2CH_3{\cdot}CH_3$	−0.42
$H{:}CH_3 - 1/2H{:}H - 1/2CH_3{:}CH_3$	0.47

B. Bond and interaction energies

	ΔH, kcal.
$1/4C{=}C + H + 1/2H{\cdot}H + 1/2H{:}H$	−132.85
$1/4C{=}C + CH_3 + 1/2CH_3{\cdot}CH_3 + 1/2CH_3{:}CH_3$	−120.09
$H{\cdot}CH_3 - 1/2H{\cdot}H - 1/2CH_3{\cdot}CH_3$	0.30
$H{:}CH_3 - 1/2H{:}H - 1/2CH_3{:}CH_3$	−0.75

Similar equations were used for the heats of formation given in Table IIB. The bond and interaction energies are listed in Table IVB. The data in this table were used in equations of the type 4 to calculate molar susceptibilities and heats of formation. The results are given in Tables IB and IIB, columns four. The agreement between the experimental and calculated values is quite good. The equations will reproduce the small differences between the *cis-*, *trans-* and 1,1-isomers.

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Pyrolysis of Mixtures of Ethane and Ethane-d_6[1]

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The pyrolysis of 50–50 mixtures of ethane and ethane-d_6 has been investigated between 510 and 610° by mass spectrometric analyses of the products. The extensive isotopic mixing that is observed in the products indicates that free radicals and hydrogen atoms occur in the decomposing mixture. The presence of nitric oxide inhibits the reaction rate and decreases the extent of isotopic mixing. It seems probable that part of the NO-inhibited reaction proceeds *via* an intramolecular mechanism. and part *via* a free-radical mechanism. In the mixtures of C_2H_6 and C_2D_6, the over-all decomposition rate of the light ethane is about 50% faster than that of the heavy ethane. This factor is in reasonable agreement with a value based on the dominant influence of the difference in zero-point energies of C–H and C–D bond vibrations. The production of CD_3 radicals from C_2D_6 is about five times faster than the production of CH_3 radicals from C_2H_6. This effect is due primarily to the greater density of rotational states of CD_3 as compared to CH_3. which lowers the activation entropy for heavy-radical formation.

The thermal decomposition of ethane has been studied by many workers since the first investigation by Pease,[2] yet it cannot be said that the reaction is satisfactorily understood. One outstanding problem concerns the proportion of the reaction that proceeds *via* a free-radical mechanism and the proportion that proceeds *via* a molecular rearrangement. In an attempt to elucidate this problem, the pyrolysis of mixtures of C_2H_6 and C_2D_6 has been followed by mass-spectrometric analyses of the products.

Experimental

The ethane used had a purity of better than 99%. The ethane-d_6 was prepared by deuteration[3] of C_2D_2 with D_2 over a nickel–asbestos catalyst. The C_2D_2 was a product of the action of 99.8% D_2O on calcium carbide previously baked for 48 hr. at 1200° under high vacuum. Mass spectrometric analysis showed the ethane component to be greater than 99% C_2D_6, but there was an admixture of 3% deuterated propane and butane.

The C_2H_6 and C_2D_6 were mixed in approximately equal amounts in 25-ml. reaction vessels. The initial pressure was about 600 mm. at the reaction temperature. In some experiments nitric oxide was added to the reaction mixture. Vessels of Pyrex, quartz, and KCl-coated Pyrex were used; they were cleaned between successive runs by heating in air for 12 hr. at 500°. After being sealed while the reactants were chilled in liquid nitrogen, the vessels were introduced into a muffle furnace regulated to ±5°. Vessels were withdrawn from the furnace at intervals, and the products admitted directly to the mass spectrometer (Consolidated) by breaking an attached capillary. The analyses were performed by the Mass Spectrometer Section of the National Bureau of Standards.

Results

Pyrolysis of C_2H_6 Alone.—A number of runs were made with C_2H_6 in various reaction vessels, and in the presence and absence of nitric oxide. Even at large conversions, the products were almost entirely H_2, C_2H_4 and CH_4. A few tenths of one per cent. of C_3H_6 and C_3H_8 were detected; C_4 and C_5 hydrocarbons were virtually absent. Typical analytical results are shown in Table I. In the packing experiments Pyrex-glass wool was used to increase the surface to volume ratio by a factor of about 50. It may be noted that at 615°

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[1] Presented in part at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] R. N. Pease, THIS JOURNAL, **50**, 1779 (1928). A review of subsequent work is given by E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 90–103.

[3] The deuterium and deuterium oxide used in this investigation were supplied by the Stuart Oxygen Company, and obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission.