[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

# Raman Spectrum of O-Methyl Isourea Hydrochloride

BY JOHN T. EDSALL

In connection with other studies from this Laboratory on Raman spectra of guanidine and urea derivatives,[1] it was of interest to determine the spectrum of the cation of O-methyl isourea, $CH_3O\text{-}C(NH_2)_2^+$. A sample of O-methyl isourea hydrochloride was supplied by Dr. J. P. Greenstein,[2] and recrystallized twice from alcohol and ether; Cl found 31.97; calcd., 32.09%. The Raman spectrum was determined on a solution containing 50% by weight of the hydrochloride in water. The solution was extremely clear and gave an excellent spectrum (Table I). The methods of exciting and measuring the spectra have already been described.[3]

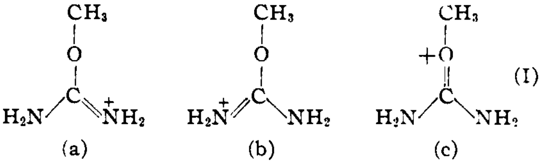
TABLE I

RAMAN SPECTRUM OF $CH_3OC(NH_2)_2^+Cl^-$ IN WATER

330 (1b) (e)
513 (4) (k, ±e)
600 (3) (k, e)
881 (10b) (k, f, e)
1077 (7b) (k, i, e)
1158 (1) (k, e)
1208 (3) (k, e)
1463 (4) (k, e)
1545 (1b) (e)
1658 (1b) (e)
2841 (2) (k)
2901 (1) (k)
2963 (7) (k, i, e)
3053 (6) (k, i, e)

Numerals in parentheses indicate intensities; "b" following a numeral indicates a broad line. The letters k, f, i and e denote the mercury lines (Kohlrausch's notation) observed to excite the Raman lines in question.

The structure of the cation of O-methyl isourea is presumably determined by resonance between the structures a, b and c in I below.



(I)

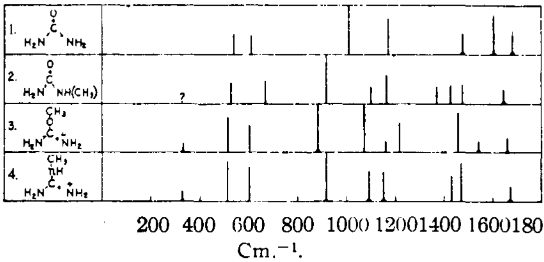


Fig. 1.—Raman spectra of 1, urea; 2, N-methyl urea; 3, cation of O-methyl isourea; and 4, the methyl guanidinium ion. Only one of the possible resonating forms is shown in the formula for each structure. The very small marks in spectrum No. 4 indicate the frequency scale, and do not denote Raman lines.

The structures a and b, which probably make a more important contribution than c to the actual configuration of the ion are, of course, completely equivalent. Therefore, the resonance energy of the structure should be high. On the other hand, in the free base, O-methyl isourea, which is formed from (I) by the loss of a proton from one of the $NH_2$ groups, all of the three resonating structures analogous to those shown for (I) are different; hence the resonance energy should be considerably less. Thus resonance tends to stabilize the cation (I), which is therefore a very weak acid with a $pK$ value[4] of 9.7. In urea, on the other hand, resonance favors the basic form, and the $pK$ value of the acid conjugate to urea is probably much less than zero.[5] Thus O-methyl isourea is a stronger base than urea (or N-methyl urea) by a factor of more than $10^{10}$.

The closest analog to the structure of (I) is probably the methylguanidinium ion,[1] which differs from it only by the replacement of the oxygen atom in (I) with an NH group. The Raman spectra of the two ions are indeed extremely similar, as is shown in Fig. 1; and the spectrum of N-methyl urea is also very similar in type, as might be expected from its close structural relation to these two ions.

The four frequencies between 2800 and 3100 cm.$^{-1}$ probably all arise from the methyl group.[6] The Raman spectrum of the principal water band in the region 3200–3600 was, of course, clearly visible on the photographs, but no lines were found which could be definitely allocated to N–H valence frequencies.

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[1] J. T. Edsall, *J. Phys. Chem.*, **41**, 133 (1937); J. W. Otvos and J. T. Edsall, *J. Chem. Phys.*, **7**, 632 (1939).

[2] J. P. Greenstein, *J. Biol. Chem.*, **109**, 529, 541 (1935); *J. Org. Chem.*, **2**, 480 (1938).

[3] J. T. Edsall, *J. Chem. Phys.*, **4**, 1 (1936); **5**, 225, 508 (1937).

[4] W. M. Bruce, THIS JOURNAL, **26**, 457 (1904); M. Zief and J. T. Edsall, *ibid.*, **59**, 2245 (1937).

[5] See the discussion of acid and base strengths by L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Ithaca, N. Y., 1940, pp. 201–214.

[6] See J. T. Edsall and H. Scheinberg, *J. Chem. Phys.*, **8**, 520 (1940).

## Summary

The Raman spectrum of O-methyl isourea hydrochloride in water has been determined. The observed spectrum is essentially that of the cation (conjugate acid) of O-methyl isourea. The structure of this ion is briefly discussed, and its similarity to the methylguanidinium ion is pointed out.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF QUEEN'S UNIVERSITY]

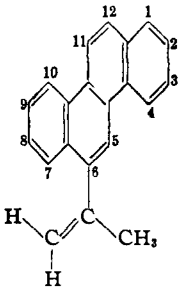
# The Ultraviolet Absorption Spectra of Some Derivatives of Chrysene

BY R. NORMAN JONES

The ultraviolet absorption spectra of numerous alkyl derivatives of polynuclear aromatic hydrocarbons have been recorded,[1] including those of several alkyl chrysenes.[2,3] Comparatively little is known, however, regarding the modifications which are produced in the spectra of polynuclear aromatic hydrocarbons by the introduction of substituents containing functional groups.

The absorption spectra of some derivatives of chrysene, synthesized by Bergmann and Eschinazi,[4] have recently been determined in this Laboratory and are recorded in Figs. 1–3 and Tables I and II.

**6-Isopropenylchrysene.**—The spectrum of 6-isopropenylchrysene (I) is illustrated in Curve A of Fig. 1 and, in Table I, the positions and intensities of the maxima are compared with similar data for 6-methylchrysene.[3] It is apparent that the introduction of the ethylenic group into the side chain makes practically no difference in the spectrum, although the ethylenic double bond is in a position indicative of conjugation with the aromatic ring system.



(I)

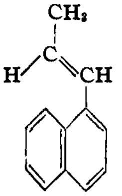
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF 6-ISOPROPENYLCHRYSENE AND 6-METHYLCHRYSENE, COMPARISON OF THE WAVE LENGTHS AND INTENSITIES OF THE MAXIMA (SOLVENT ETHANOL)

| 6-Isopropenylchrysene | | 6-Methylchrysene[3] | |
|---|---|---|---|
| Wave length, Å. | Intensity, log $E_{molar}$ | Wave length, Å. | Intensity, log $E_{molar}$ |
| 2220 | 4.45 | .. | .. |
| 2430 | 4.30 | .. | .. |
| 2600 | 4.80 | 2600 | 4.90 |
| 2695 | 5.09 | 2695 | 5.18 |
| 2850 | 4.02 | 2850 | 4.02 |
| 2980 | 4.02 | 2970 | 4.08 |
| 3100 | 4.11 | 3095 | 4.15 |
| 3235 | 4.13 | 3230 | 4.13 |
| (3450)[a] | 3.06 | 3460 | 3.03 |
| (3530)[a] | 2.75 | 3530 | 2.63 |
| 3630 | 2.88 | 3620 | 3.03 |

[a] Inflection only.

The introduction of a vinyl group into benzene causes a profound alteration of the absorption, as exemplified by styrene,[5] and the spectrum of 1-propenylnaphthalene[6] (II) shows a complete loss of fine structure and a bathochromic shift of about 200 Å. compared with 1-methylnaphthalene.[7]



(II)

If a vinyl substituent is to modify the electronic activation of a polynuclear aromatic hydrocarbon, it must do so by altering the nature and the relative contributions of the several canonical forms which participate in the ground and activated electronic states. Presumably, in the case of styrene, this will involve principally dipolar quinonoid structures such as IIIa and IIIb. Similar quinonoid structures may be written for the vinyl derivatives of complex polynuclear

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(1) Jones, *Chem. Rev.*, **32**, 1 (1943).

(2) Jones, THIS JOURNAL, **63**, 313 (1941).

(3) Brode and Patterson, *ibid.*, **63**, 3252 (1941).

(4) Bergmann and Eschinazi, *ibid.*, **65**, in press (1943).

(5) Arends, *Ber.*, **64**, 1936 (1931).

(6) Pestemer and Wiligut, *Monatsh.*, **66**, 119 (1935).

(7) de Laszlo, *Z. physik. Chem.*, **118**, 369 (1925).