# The Absorption Coefficients of the Acetyl Halides

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# LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.*

## The Absorption Coefficients of the Acetyl Halides

The absorption coefficients of acetyl chloride, bromide and iodide for some of the lines of the mercury arc spectrum have been measured with a thermopile and monochromator. The values obtained are listed in Table I. The long wave-length limits for the absorption, as estimated by an extrapolation of these data, are 2900, 3100, and 4000A for the chloride, bromide, and iodide, respectively. The absolute values of the absorption coefficients and these limits may be in error a few percent because of the reactivity of the compounds and, in the case of the chloride and iodide, the separation of condensed phases as the result of the reaction occurring.

Preliminary analyses of the products formed in the decomposition of these compounds caused by the absorption of ultraviolet light indicate that the reactions involved are quite complex. No hydrogen, ethane, or ethylene was detected by suitable tests for each.[1] The non-condensable (in liquid air) gases consisted of carbon monoxide and methane. The non-condensable portion obtained from acetyl chloride on illumination with $\lambda = 2537A$ was 60 percent carbon monoxide and that obtained from the bromide or iodide was approximately 90 percent carbon monoxide. The condensable products contained the corresponding methyl halide but otherwise showed marked variations.

In the case of acetyl chloride a liquid product separated out during the course of the illumination. This substance appeared first as a white mist which became yellow as it settled on the walls and finally it changed to a dark brown. The presence of some hydrogen chloride and unchanged acetyl chloride interfered with the analysis of the liquid but the carbon and hydrogen percentages were found to be in fair agreement with the hypothesis that this substance is a polymer of either diacetyl or ketene. Tests of water solutions of the condensable gases for carbonate and oxalate (from ($COCl_2$) ions) were negative.

Acetyl bromide did not yield a liquid such as was obtained from the chloride. In addition to methyl bromide the condensable products contained some bromine and compounds containing more than one atom of bromine per molecule, probably ethylene bromide. The products from acetyl iodide contained considerable quantities of free iodine and some liquid which was not analyzed on account of the small amount obtained.

Detailed studies of the decomposition of these three compounds are in progress.

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[1] Blacet and Leighton, Ind. Eng. Chem. Anal. Ed. **3**, 266 (1931); Blacet, MacDonald and Leighton, ibid. **5**, 272 (1933); Blacet and MacDonald, ibid. **6**, 334 (1934); Blacet and Volman, ibid. **9**, 44 (1937).

TABLE I. *Absorption coefficients.*

| Wave-length A | Acetyl chloride | Acetyl bromide | Acetyl iodide |
|---|---|---|---|
| 2537 | 21.6 | 64.8 | 468 |
| 2652 | 10.3 | 46.8 | 324 |
| 2699 | 9.2 | 30.6 | — |
| 2753 | 4.5 | 12.6 | 216 |
| 2804 | 2.9 | 5.0 | — |
| 2894 | — | — | 126 |
| 3130 | — | — | 46.8 |
| 3650 | — | — | 6.5 |

$\epsilon = 1/cl \log_{10} I_0/I$ (c in moles/liter, l in cm)

## Raman Frequencies of Hexamethylene Glycol

In the course of preparation of a series of glycols, Mr. George W. Anderson of the Department of Chemistry of this University supplied the writer with a specimen of hexamethylene glycol ($HO \cdot (CH_2)_6 \cdot OH$), with a melting point of 40.9 deg. C, and a boiling point range of 135.5 to 136.5 deg. C at a pressure of 8 mm Hg.

In determining the Raman frequencies for this compound, mercury arcs in pyrex were used for excitation. In some runs a filter consisting of a saturated solution of sodium nitrite was used to eliminate the Raman lines resulting from the mercury 4047A group of lines. An iron spark spectrum adjacent to the Raman spectrum was used for the purpose of interpolating the wave numbers of the Raman lines.

The values are as follows, with estimated relative intensities and mercury line sources according to the Kohlrausch designations:

814 (2-*e*), 852 (2-*e*), 874 (2-*e*), 915 (1-*e*), 1000 (2-*e*), 1052 (3-*e*), 1084 (3-*e*), 1298 (4-*ek*), 1435 (4-*ekc*), 1472 (4-*ekc*), 2855 (8-*ek*), 2905 diffuse (8-*ek*).

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