for the above measurements changed with time; freshly prepared solutions were measured within 5 minutes of mixing and corrected to zero time using the following observed increases in D per 5-minute interval: 475 mμ, 1%; 500 and 525 mμ, 2.5%. Other small corrections were: (1) using 21 for K_{11}, a rather than its first approximation, a_0, has been used in applying equation (2); (2) the values of a and of the contribution of Fe^{III} to the optical density have been corrected for the hydrolysis[8] of Fe^{+3} to $FeOH^{++}$.

The extinction coefficients of the complex $FeFe(CN)_6$, for 280–550 mμ, given in Fig. 1 were calculated from the absorption spectrum of a solution that was 0.00705 F in $Fe(ClO_4)_3$, 0.0056 F in $K_3Fe(CN)_6$ and 0.50 M in $HClO_4$. The concentration of $FeFe(CN)_6$ of 1.01 (±0.02) $\times 10^{-3}$ M in this solution, calculated from the optical densities at 475, 500 and 525 mμ and the extinction coefficients of Table I, corresponds to a K_{11} of 36 in 0.50 M $HClO_4$.

A second set of data was obtained for $b_0 > a_0$ where one should consider the complexes $Fe(Fe(CN)_6^{-3})_j^{3-3j}$. These solutions at 26 ± 2° and at an ionic strength of 1.00 contained $Fe(ClO_4)_3$, $K_3Fe(CN)_6$, $NaNO_3$ and 0.102 M HNO_3, since potassium perchlorate precipitated from solutions in which sodium perchlorate and perchloric acid were used to maintain the acidity and ionic strength.

Figure 2 shows that (a_0b/D_c) is a linear function of b; the parameters of the straight lines are given in Table II. The apparent values of $\epsilon_{11}K_{11}$ and K_{11} are smaller than those of Table I; an attempt has been made to resolve this discrepancy by considering the formation of $FeNO_3^{++}$, with formation constant N, so that $(FeNO_3^{++}) = Na(NO_3^-)$. Because the ionic strength was 1.0, $(NO_3^-) + 6b_0 = 1$. The equation that results is

TABLE II

COMPLEXING OF Fe^{+3} BY EXCESS $Fe(CN)_6^{-3}$ IN NITRATE SOLUTIONS

λ, mμ	(Intercept)$^{-1}$ $\times 10^{-3}$	Slope/ intercept	N	K_{11}
475	12.9	11.8	0.35	17
500	9.4	10.2	.26	15
525	6.25	8.2	.36	12.5

$$(\epsilon_{11}K_{11})(a_0b/D_c) = 1 + N + b\left(K_{11} - 6N - \frac{\epsilon_{12}K_{12}}{\epsilon_{11}K_{11}}\right) + b^2$$

Accepting equation (3) and the values of $\epsilon_{11}K_{11}$ of Table I, the intercepts recorded in Table II have been used to calculate N. From the ratio of slope to intercept one can then calculate K_{11} (neglecting the $\epsilon_{12}K_{12}/\epsilon_{11}K_{11}$ term). The results for N agree as well as can be expected. The average deviation of the K_{11} values is greater than that of Table I, and the average (15) is 25% less than that of Table I. These discrepancies and the trend in the calculated values of K_{11} with wave length may be due to contributions of the $(\epsilon_{12}K_{12}/\epsilon_{11}K_{11})$ term. We feel that all of the results are sufficiently concordant to indicate the essential validity of the interpretations given here.

Experimental.—$Fe(ClO_4)_3 \cdot 10H_2O$ was prepared by evaporation of a mixture of $FeCl_3 \cdot 6H_2O$ with excess 60% $HClO_4$ and recrystallization. It was free of Cl^- and ClO_3^-. Iron(III) was determined as recommended by Swift.[9] Ferro- and ferricyanide solutions were prepared from recrystallized $K_4Fe(CN)_6 \cdot 3H_2O$ and $K_3Fe(CN)_6$ and were determined as recommended by Swift.[10]

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[8] Using 10^{-3} for the hydrolysis constant, E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[9] E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

[10] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 438–441.

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Shifted Position of Infrared Absorption Bands Associated with the C=O Linkages in Polycyclic Compounds

BY MARIE LOUISE JOSIEN AND NELSON FUSON

Although a great deal of research has been made on the Raman and infrared band assigned to the C=O stretching vibration in long chain and single ring compounds, spectroscopic study of the C=O linkage in polycyclic compounds is still relatively unexplored. Among the studies which have been made in this latter field may be cited those of Dulou,[1] Kohlrausch,[2] Biquard,[3] Lecomte,[4] Flett,[5] R. N. Jones,[6] and Josien and Fuson.[7] In the course of an infrared spectroscopic study of some polycyclic hydrocarbons and their oxidation products the following values for the carbonyl group absorption bands have been obtained which we believe have not yet been reported in the literature:

Compound[8]	Wave length (in microns) of band assigned to the C=O stretching vibration
Pyrenequinone-3,8	6.10
Pyrenequinone-3,10	6.10
Acetylpyrene	6.02
Chrysenequinone-1,2	6.03
Acenaphthenequinone	5.63 and 5.79
9-Fluorenone-1-carboxylic acid	5.73 and 6.00

These spectral wave length values were obtained for crystalline samples prepared in paraffin oil paste form. A comparison of these results with other results given in the literature cited suggests the following comments: (a) We have assigned the two bands, 5.73 μ and 6.00 μ, of 9-fluorenone-1-carboxylic acid to the carboxylic acid C=O and the cyclic ketone C=O, respectively. The first assignment is in agreement with the usual band location for carboxylic acids[9]; the second is without doubt located at such a position because of the effect of conjugation. (b) From the appearance of two bands, 5.63 μ and 5.79 μ, in acenaphthene-

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(1) Dulou, Thèse, 1933, Bordeaux, France.

(2) Kohlrausch, *Z. Elektrochem.*, **43**, 282 (1937).

(3) Biquard, *Bull. soc. Chim. France*, **7**, 895 (1940); **8**, 55, 725 (1941).

(4) J. Lecomte, *J. Phys.*, **6**, 259 (1945).

(5) Flett, *J. Chem. Soc.*, 1441 (1948).

(6) R. N. Jones, *et al.*, THIS JOURNAL, **70**, 2024 (1948); **71**, 241 (1949); **72**, 86 and 956 (1950).

(7) M. L. Josien and N. Fuson, *Compt. rend.*, in press.

(8) These compounds were prepared by Dr. St. Elmo Brady, Professor of Chemistry, Fisk University, Nashville, Tennessee.

(9) H. M. Randall, R. G. Fowler, N. Fuson and R. Dangl, "Infrared Determination of Organic Groups," D. Van Nostrand Co., New York, N. Y., 1949, p. 20.

quinone, it would appear that because of the symmetry of this molecule, interaction between the two keto-group vibrations occurs to produce two separate regions of absorption in a way similar to that well known for normal and cyclic anhydrides. In the chrysenequinone, however, even though the carbonyl bonds are adjacent, only one band attributable to the C=O vibration was observed. (c) The relative position of the bands associated with the carbonyl vibration in the two pyrenequinones (6.10 μ) and acetylpyrene (6.02 μ) are almost identical to that of *p*-benzoquinone (6.01 μ) and acetophenone (5.92 μ),[10] the carbonyl attached directly to the ring in each case being shifted almost 0.1 μ to longer wave lengths than that for the carbonyl in a side chain. The presence of a C—C linkage between the conjugated nucleus and the carbonyl group appears to diminish the shifting effect of conjugation. (d) The location of the absorption due to the pyrenequinones is about 0.1 μ to longer wave lengths than that previously recorded for keto-type C=O groups, conjugated or not conjugated, in oxidation products of hydrocarbons.[1–6] This may have a relation to the size of these highly conjugated molecules, for theoretical studies of bond fixation in compounds containing the carbonyl group led Coulson[11] to state that "...the larger the molecule in general the less fixed are the bonds; in other words the more like a metallic conductor does the system become...."

These results from the examination of the location of the infrared band associated with the carbonyl group in highly conjugated polycyclic compounds are evidence of the interest of this sort of study. Much work is necessary, however, before general conclusions on the mechanism of the band shifting can be drawn. This investigation forms a part of a research project supported by a research grant from the division of Research Grants and Fellowships of the National Institutes of Health, United States Public Health Service.

[10] *Ibid.*, pp. 165–166.

[11] C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106 (1946).

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Enrichment of Antimony Activity through the Szilard–Chalmers Separation[1]

BY MILTON KAHN[2]

The two stable isotopes of antimony, Sb^{121} and Sb^{123}, capture thermal neutrons to form 2.8-day Sb^{122} and 60-day Sb^{124}, respectively.[3] Williams[4] reported that triphenylstibine is a suitable compound for the enrichment of the antimony activity through the Szilard–Chalmers separation. This reaction had previously been independently investigated by the author and in view of the fact that Williams did not give experimental details or enrichment factors it was thought worth while to report the results obtained by the author.

A solution of triphenylstibine in benzene was irradiated with thermal neutrons. Several portions of this solution were then extracted with various aqueous solutions. In each case a large fraction of the total antimony activity appeared in the aqueous phase associated with a small amount of inactive antimony. The results are summarized in Table I.

TABLE I

Aqueous soln.	Enrichment factor[a]	Sb/activity in aq. phase, %
H_2O	200	47
2.5 f HCl	200	54
6 f HCl	600	65
3 f NH_4OH	300	85
1 f NaOH	300	88

[a] Specific activity of antimony in aqueous phase divided by specific activity of antimony in benzene phase before extraction.

The appearance of as much as 1 mg. of antimony in the various aqueous solutions suggested that the triphenylstibine was initially contaminated with antimony in a water-soluble state. Accordingly, an experiment was carried out wherein a benzene solution of triphenylstibine was washed with 2.5 f hydrochloric acid prior to irradiation. In this case 58% of the antimony activity was enriched by a factor of 6000.

Composite decay curves of the antimony activity in the benzene phase and the aqueous phase of the foregoing experiment were obtained over a period of 36 days, zero time being approximately 3 days after the irradiation. An analysis of these curves, assuming that the long-lived component of each composite decay curve was 60-day Sb^{124}, revealed that they were made up of two components, the shorter lived component in each curve having a 2.8-day half-life. It was found that the same fraction of the total antimony activity appeared in the aqueous phase regardless of whether the calculations were based on the Sb^{122} activity or on the Sb^{124} activity. This suggests that this particular Szilard–Chalmers reaction is the same for both isotopes of antimony.

Experimental

Triphenylstibine obtained from Eastman Kodak Co. was used without further purification. A 0.75 f solution of triphenylstibine in thiophene-free benzene was irradiated with neutrons produced in the Washington University cyclotron. Paraffin blocks were placed around the solution in order to slow down the neutrons. Five ml. of the irradiated solution was transferred to a separatory funnel, diluted to 25 ml. with thiophene-free benzene, and extracted with 40 ml. of a given aqueous solution. A 5-ml. portion of the benzene phase, a 5-ml. portion of the aqueous phase, and a 5-ml. portion of the original active benzene solution were transferred to separate six-inch Pyrex test-tubes. Each tube was then counted in a reproducible geometry with a thick-walled Geiger-Mueller counter, the gamma radiation associated with the decay of Sb^{122} and Sb^{124} being detected. The activity determined in each case was of the order of 1000 counts per minute. In all experiments the sum of the activity in each phase equalled the total activity initially present in the benzene solution before extraction within a probable error of 4%. The stability of the Geiger-Mueller counter was checked from day to day with a gamma-ray standard which consisted of a sealed tube containing a solution of cobalt chloride with approximately 1000 counts per minute of 5.3-year Co^{60} activity.

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[1] Presented before the Thirty-First Annual Meeting of the New Mexico Academy of Science, Physical Science Section, at Albuquerque, October, 1949.

[2] Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

[3] Livingood and Seaborg, *Phys. Rev.*, **52**, 135 (1937).

[4] Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).