TABLE I

Oxime	Product	Temp., °C.	Yield, %	M.p., °C.	Reported m.p., °C.	Procedure
Benzophenone	Benzanilide	130	99–100	161–162	162–163	A
p,p'-Dimethoxybenzophenone	Anisoylanisidine	130	91	199–203	202	A
Acetophenone	Acetanilide	95	97	103–106	114	A
p-Methoxyacetophenone	*p*-Methoxyacetanilide	120	99–100	122–124	127	A
Cyclohexanone	ε-Caprolactam	115	89	60–62	65–68	B
Cyclopentanone	δ-Valerolactam	130	74	31–35	39–40	B

circumstances different from those which might be expected for a general acid-catalyzed reaction of oximes. In this method, the oxime is heated in polyphosphoric acid[4] at moderate temperatures ranging from 95–130°. Solution of the oxime is sometimes accompanied by mild heating effects, but no evidence of reaction is otherwise noted. Amides are formed in essentially quantitative yield; such losses as occur on isolation are apparently due to variations in physical properties of the products.

This procedure, described briefly in the experimental section, may be illustrated by the case of benzophenone oxime, the compound originally investigated by Beckmann. There are no isomeric forms of the ketoxime; the product is crystalline, easily isolated, and has a well-defined melting point. With polyphosphoric acid, the rearrangement of the oxime was accomplished in ten minutes at 130°; the clear solution was diluted with water to yield crystalline benzanilide in 99–100% yield; the melting point and infrared spectrum showed no impurities in amounts which would affect these two properties.

Other examples are given in Table I. The reaction is satisfactory for oximes of diaryl ketones, alkylaryl ketones and aliphatic ketones of the cyclic type. When the products are soluble in the aqueous phosphoric acid resulting after treatment of the mixture with water, special isolation methods are necessary and the yields are lowered.

It is not possible to describe the precise course of the reaction. A phosphate ester of the oxime may be involved as an intermediate. Dehydration of the products does not occur, although the reagent is also a strong dehydrating agent. The rearrangement is probably initiated by acid catalysis, but here polyphosphoric acid is the solvent and proton donor as well. Other examples of the Beckmann rearrangement are currently under investigation, and while these studies are not completed, we have observed that in cases of so-called abnormal Beckmann reactions our products do not correspond to those previously reported.

While exceptions may possibly be found to the generality of the method described here, our results at present indicate that polyphosphoric acid may be the reagent of choice for the rearrangement.

Experimental

General Procedure A.—A mixture of 2.00 g. of the oxime and 60 g. of polyphosphoric acid was heated with manual stirring to the indicated temperature (Table I). The resulting solution was maintained at the specified temperature for ten minutes and then poured into 300 ml. of water. The water solution was extracted with 1:1 ether–ethyl acetate. The organic layer was washed with water, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The product was isolated by filtration and evaporation of the solvents to give the crude yields reported in Table I. All crude products were colorless crystalline materials; melting points are given for the crude material as an indication of purity; identity was confirmed before and after recrystallization.

General Procedure B.—The initial reaction was conducted according to Procedure A. The products may be extracted from water only with difficulty, and it was therefore necessary to follow the isolation procedure essentially as given in reference 5.

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[4] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2962, 2965 (1950).

[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 371.

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The Absorption of Radiation by Inhomogeneously Dispersed Systems

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RECEIVED JANUARY 12, 1952

Because of a lack of suitable solvents, a great deal of qualitative infrared analysis is performed on solid preparations. To control sample thickness and minimize light scatter, the absorbing material is usually pressed out as a film, deposited from solution on a silver chloride or sodium chloride plate or mulled with a mineral oil or with perfluorokerosine. A technique involving dispersion in solid potassium bromide has also been described.[1]

These techniques have also been adapted for quantitative analysis,[2–4] in spite of the difficulties inherent in the preparation of films or mulls of reproducible optical quality. Quantitative results can be obtained by the use of empirical calibration curves derived from measurements on standard samples, but it is the object of this communication to emphasize that when the absorbing material is agglomerated into macro particles, separated by regions of high transmittance, or when variations occur in the thickness of the sample in the beam, the laws governing the absorption of radiation by isotropic material are no longer applicable. These limitations are inherent in the absorption laws themselves; they apply where the particles are large in comparison with the wave length of the light, and are additional to the scattering effects of reflection and refraction at the boundaries of the absorbing areas, which have been discussed by Pfund,[5] Henry[6] and others.

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[1] M. M. Stimson, Abstracts of Symposium on Molecular Structure and Spectroscopy, Ohio State University, June, 1951, p. 59.

[2] R. B. Barnes, R. C. Gore, E. F. Williams, S. G. Linsley and E. M. Patterson, *Anal. Chem.*, **19**, 620 (1947).

[3] H. L. Dinsmore and D. C. Smith, *ibid.*, **20**, 11 (1948).

[4] J. D. Sands and G. S. Turner, Abstracts XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., 1951.

[5] A. H. Pfund, *J. Opt. Soc. Am.*, **23**, 375 (1933); **24**, 143 (1934).

[6] R. L. Henry, *ibid.*, **38**, 775 (1948).

The Bouguer–Lambert–Beer Relationship.—The absorption of radiation by a solute molecularly dispersed in a non-absorbing solvent is commonly expressed by the Bouguer–Lambert–Beer equation

$$E_t = \frac{1}{cl}\log_{10}\left(\frac{I_0}{I}\right)_\nu \qquad (1)$$

where E_t is the (true) molecular extinction coefficient, c the concentration of the solute in moles per liter of solution, l the path length of the radiation in the solution in cm., I_0 the intensity of a parallel beam of monochromatic radiation of frequency ν entering normally into the solution, and I the energy of the transmitted radiation.

This relationship is valid only for strictly limited conditions; variation of E_t with c is recognized to occur quite commonly, and the effects resulting from the use of non-monochromatic radiation have been the subject of a recent study.[7,8]

In a film or mull in which the particles are aggregated, it may be assumed that a fraction χ of the total energy incident on a given volume element of the absorbing system passes through the absorbing particles while the remainder of the radiation $(1 - \chi)$ passes through the freely transmitting spaces between the particles. If the effects of scatter and diffraction at the surfaces of the absorbing particles are neglected, such a system will be equivalent optically to that illustrated in Fig. 1, where the given volume element is divided into separate absorbing and transmitting parts in the ratio of χ to $(1 - \chi)$. Here χI_0 and I' are the energies incident on, and transmitted by the absorbing particles and $(1 - \chi)I_0$ the energy passing through the clear spaces between the particles without loss by absorption.

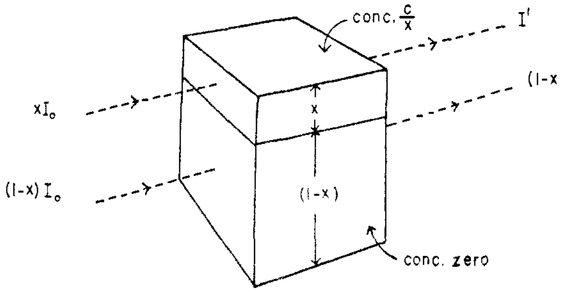

Fig. 1.—Radiation absorbed by inhomogeneously dispersed systems.

If it be assumed further that Beer's law is obeyed during the absorption, we may write for the upper section of the volume element

$$E_t = \frac{\chi}{cl}\log_{10}\left(\frac{\chi I_0}{I'}\right)_\nu$$

whence, if

$$\epsilon_t = 2.303E_t$$

$$I' = \chi I_0\, e^{-\epsilon_t \frac{cl}{\chi}} \qquad (2)$$

If E_χ is the experimentally observed molecular extinction coefficient as evaluated from a measurement on the whole volume element

$$E_\chi = \frac{1}{cl}\log_{10}\left(\frac{I_0}{I' + (1 - \chi)I_0}\right)$$

and

$$I_0\, e^{-\epsilon_\chi cl} = I' + (1 - \chi)I_0 \qquad (3)$$

where

$$\epsilon_\chi = 2.303E_\chi$$

Substituting for I' from (2) and dividing by I_0 we obtain

$$e^{-\epsilon_\chi cl} = (1 - \chi) + \chi e^{-\epsilon_t \frac{cl}{\chi}} \qquad (4)$$

Since ϵ_t is a constant, and

$$\epsilon_t cl = 2.303 \log_{10} (I_0/I)\nu$$

equation (4) may be solved numerically for selected values of χ, and E_χ/E_t evaluated at various optical densities.

The results of such a computation covering the range of χ from 0.05 to 0.99 at optical densities between 0.1 and 2.0 are summarized in Table I.

Magnitude of the Effect.—For all values of χ and at all optical densities, E_χ is less than E_t, and for a given value of χ the difference between E_χ and E_t is greater the higher the optical density. From a plot of E_χ/E_t against χ it can be readily shown that the curve slopes steeply for large values of χ. This is of importance since it is at high values of χ that the conditions approach most closely to a homogeneous dispersion. In mulls and films the presence of quite small freely transmitting areas may therefore result in significant differences between "true" and "experimental" extinction coefficients and optical densities. Thus with 10% of freely transmitting space in the sample and a true optical density of 1.0 there would be an error of 22.5%, and at a true optical density of 1.5 the error would be 39%. Measurements at such high true optical densities may well occur in practice since they correspond to experimentally observed optical densities of 0.775 and 0.91, respectively, which lie within the normal range of convenient measurement.

At lower values of χ, where the proportion of freely transmitting space is larger, the evaluation of E_t from E_χ becomes indeterminate even when χ is known. From the plots of $E_\chi cl$ against $E_t cl$ shown in Fig. 2 it is observed that as $E_t cl$ increases, $E_\chi cl$ levels off asymptotically. The curve becomes

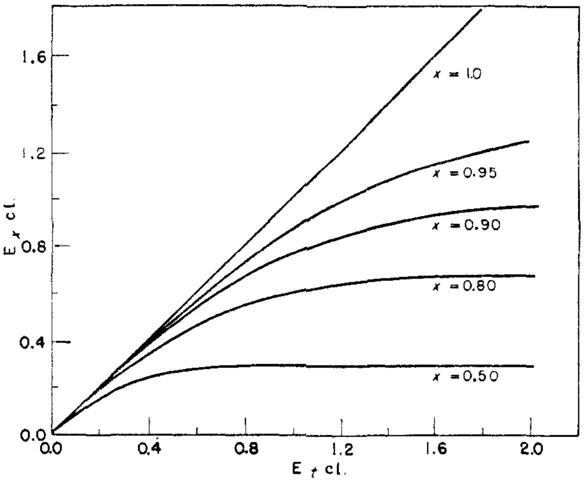

Fig. 2.—Absorption of radiation by inhomogeneously dispersed systems.

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(7) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

(8) R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, *ibid.*, **74**, 80 (1952).

TABLE I

VALUES OF E_χ/E_t IN TERMS OF THE FRACTIONAL ABSORBING SPACE (χ) AND THE TRUE OPTICAL DENSITY ($\log_{10}(I_0/I)\nu$

For the significance of the italicized figures see text.

χ	E_χ/E_t															
0.05	0.220	*0.110*	*0.075*	*0.055*	*0.045*	*0.040*	*0.035*	*0.030*	*0.025*	*0.020*	*0.020*	*0.020*	*0.020*	*0.015*	*0.015*	*0.010*
.10	.430	.230	*.160*	*.115*	*.090*	*.075*	*.060*	*.055*	*.050*	*.045*	*.040*	*.035*	*.030*	*.030*	*.030*	*.025*
.20	.645	.430	.315	*.240*	*.190*	*.160*	*.135*	*.120*	*.105*	*.095*	*.085*	*.080*	*.075*	*.070*	*.065*	*.050*
.30	.760	.585	.450	.365	*.305*	*.255*	*.220*	*.195*	*.170*	*.155*	*.140*	*.130*	*.125*	*.110*	*.105*	*.075*
.40	.850	.690	.580	.485	.415	.355	.310	*.275*	*.245*	*.220*	*.205*	*.185*	*.185*	*.160*	*.145*	*.110*
.50	.885	.780	.680	.590	.520	.460	.410	.365	.325	*.295*	*.270*	*.250*	*.240*	*.215*	*.200*	*.150*
.60	.920	.845	.770	.690	.625	.565	.510	.460	.425	.395	.355	.325	.305	*.285*	*.265*	*.200*
.70	.960	.900	.840	.775	.720	.670	.620	.570	.525	.495	.455	.420	.390	.365	.340	.255
.80	.975	.935	.900	.860	.820	.775	.735	.695	.650	.605	.575	.535	.510	.475	.445	.345
.90	.985	.970	.955	.935	.910	.890	.860	.830	.800	.775	.750	.705	.675	.645	.610	.485
.95	.995	.990	.980	.960	.950	.940	.925	.910	.895	.870	.855	.825	.810	.775	.745	.635
.99	1.000	1.000	.995	.990	.990	.990	.990	.985	.975	.975	.970	.960	.960	.945	.935	.860
$\log_{10}(I_0/I)\nu$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	2.0

flat when the term $\chi e^{-\epsilon_t cl/\chi}$ is negligible in comparison with $(1 - \chi)$ in equation (4). The figures in Table I are italicized where the ϵ_t dependent term is less than 1% of $(1 - \chi)$; and under these conditions the absorption curve will be flat and no absorption bands detectable.

A non-uniform concentration is more likely to occur in mulls or other powder preparations than in films deposited from solution or by pressure, but in such films there may be significant differences in sample thickness at different positions in the radiation beam. For these conditions, where l is variable but c is constant, an equation identical in form with (4) may be derived, and the effects on the intensity of absorption will be comparable with those discussed above.

Significance in Ultraviolet Spectrophotometry.—The spectrophotometry of solid samples in the ultraviolet has received less attention than in the infrared, both on account of the larger selection of suitable solvents, and because of the greater magnitude of the scattering errors. However, in the application of microspectrophotometry to the study of biological cell structure[9] an inhomogeneous distribution of the absorbing material in the field of the microscope is likely to be encountered. Under these circumstances, this effect would lead to low values for the concentrations of the ultraviolet absorbing cell constituents if such concentrations are evaluated in terms of molecular extinction coefficients based on measurements made in homogeneous solution.

Concluding Remarks.—Under most experimental conditions, the difficulties of correcting adequately for the loss of light by scattering offer the most serious deterrent to the evaluation of absolute absorption intensities in non-isotropic systems, but even if adequate corrections for scattering losses could be made (as for example by the use of mulling agents of the correct refractive index) caution must still be exercised in the application to such systems of the radiation absorption laws established for true solutions. Since the effect of freely transmitting spaces in the sample varies rapidly with the (true) optical density, both the shapes and *relative* intensities of absorption bands will also be modified and this can be of significance in qualitative as well as in quantitative spectrophotometric analysis.

To simplify the mathematical treatment in the above discussion a sharp distinction has been drawn between the absorbing and the freely transmitting regions of the sample preparation, but the same conditions must exist in principle wherever a concentration gradient is present.

Acknowledgment.—Helpful discussions of this problem with Dr. H. G. Bernstein, Dr. C. Sandorfy and Dr. T. Y. Wu of the National Research Council of Canada are gratefully acknowledged.

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[9] See Discussions of the Faraday Society, No. 9, Aberdeen University Press, Aberdeen, Scotland, 1950.

Preparation of Small Quantities of Germanium Tetramethyl

BY J. H. LENGEL AND V. H. DIBELER

RECEIVED DECEMBER 15, 1951

As part of a mass spectrometric study of the Group IV tetramethyl compounds, a satisfactory method was required to prepare small amounts of germanium tetramethyl. Our experience together with that of previous investigators[1,2,3] made it apparent that the Grignard method of preparation was unsuitable for our purposes. Several Grignard preparations made in this laboratory using ethyl ether, *n*-butyl ether, "isoöctane" and tetrahydrofuran as solvents gave only traces. These low yields were principally because of the low boiling point of germanium tetramethyl (approximately 43°) and the difficulty of separation from the ethers.

Dr. Anton B. Burg pointed out to us the suitability of applying vacuum techniques to the reaction between zinc alkyls and germanium tetrachloride, first described by Winkler.[4] Accordingly, two preparations of approximately 10-millimole quantities of germanium tetramethyl were made by using zinc dimethyl and germanium tetrachloride obtained from commercial sources. Mass spectrometric analyses of these compounds showed an estimated total impurity of less than one mole per cent. in each case.

In the first preparation approximately stoichiometric quantities of zinc dimethyl and germanium tetrachloride were distilled *in vacuo* from glass storage ampoules into a

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[1] L. M. Dennis and W. I. Patnode, THIS JOURNAL, **52**, 2779 (1930), give references to earlier work.

[2] C. W. Young, J. S. Koehler and D. S. McKinney, *ibid.*, **69**, 1410 (1947).

[3] H. Siebert, *Z. anorg. allgem. Chem.*, **263**, 82 (1950).

[4] C. Winkler, *J. prakt. Chem.*, **144**, (N. F. 36, 204 (1887)).