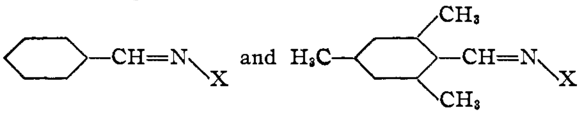
Absorption Spectra of Some Benzal and Mesitylal Schiff Bases

BY LLOYD N. FERGUSON AND JOHN K. ROBINSON

When considering the relative light absorptions of two compounds such as



where X is any simple group, it is difficult to predict whether the steric effect of the *ortho* methyl groups in the mesityl compound will decrease absorption from that of the simple phenyl compound or whether there will be an increase in absorption due to hyperconjugation of the methyl groups. For this reason, the spectra of several Schiff bases of benzaldehyde and mesitylaldehyde were measured. The spectral characteristics are listed in Table I.

TABLE I

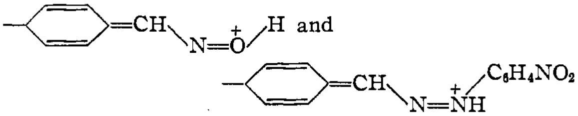
SPECTRAL CHARACTERISTICS OF SOME BENZAL AND MESITYLAL SCHIFF BASES

	Oxime		*p*-Nitrophenylhydrazone		Ethylenediamine	
Compound	λ_m (mμ)	ϵ_m	λ_m (mμ)	ϵ_m	λ_m (mμ)	ϵ_m
Benzal	252	14,300	407	34,200	247[1]	29,000[1]
Mesitylal	252	9,400	411	31,700	264	8,100
Difference	0	4,900	4	2,500	17	20,900

From these results, it is observed that there are no significant differences between the wave lengths of maximum absorption of the two oximes or of the two *p*-nitrophenylhydrazones. In going from dibenzalethylenediamine to dimesitylalethylenediamine there is a bathochromic effect. This, perhaps, is due to the hyperconjugation of the methyl groups becoming more prominent since the chromophoric system is double. Actually upon constructing the Fisher–Hirschfelder models of these three classes of compounds there appears to be only a small steric hindrance between the mesityl methyl groups and the group X.[2]

It has been observed before[3] that small steric hindrances have little effect upon $\lambda_{\max.}$ but do decrease $\epsilon_{\max.}$. This is illustrated in the present case by the oximes and the ethylenediamines. It is noted that this effect is very small in the case of the nitrophenylhydrazones; however, this is understandable. The nitrophenylhydrazones have absorption bands near 400 mu[4] without the aid of the phenyl or mesityl groups at the other end of the molecule, and consequently steric hindrance does not affect appreciably the molecular extinction.

The only explanation offered at this time for the trend in the differences of $\lambda_{\max.}$ is to say that forms such as



contribute to the resonances of benzaldoxime and benzal-*p*-nitrophenylhydrazone. Such forms would be opposed by the hyperconjugation of the methyl groups in the mesityl nucleus. It may be that the two effects just cancel one another in the mesitylaldoxime, that the hyperconjugation is slightly more effective than the opposing resonance in the mesitylal-*p*-nitrophenylhydrazone and that in the ethylenediamine compounds, where the corresponding resonant forms cannot exist and the chromophoric system is double, the hyperconjugation causes a much larger bathochromic effect.

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[1] Taken from Ferguson and Branch, THIS JOURNAL, **66**, 1467 (1944).

[2] O'Shaughnessy and Rodebush found the steric interference between the *ortho* methyl groups and the carbonyl oxygen of 2,4,6-trimethylacetophenone to be hardly strong enough to prevent a coplanar configuration, *ibid.*, **62**, 2910 (1940).

[3] O'Shaughnessy and Rodebush, *ibid.*, **62**, 2910 (1940).

[4] Ferguson and Battle, Report presented before the Organic Division of the Washington Chemical Society, Oct., 1948, at Washington, D. C.

Comparison of Age with the Relative Abundance of Argon and Potassium in Rocks

BY R. L. FARRAR, JR., AND GEORGE H. CADY

The study reported in this communication was done as a test of the proposal of Thompson and Rowlands[1] that the accumulation of argon resulting from decay by K electron capture of K^{40} should serve as a measure of the age of rocks containing potassium. For this study solid rocks of known geologic age were kindly furnished by G. E. Goodspeed of our Department of Geology.

The analytical procedure involved the following steps: (1) A 60-g. sample of sodium carbonate was freed of argon by pumping away gas for three hours from the molten salt held in a stainless steel vessel at about 950°. (2) Argon and other gases were removed from the surface of a 10-g. sample of rock composed of pea-sized pieces by allowing the material to stand for about an hour at room temperature in a vacuum. (3) The rock was then dissolved in the sodium carbonate at 950 to 1000°. This process was allowed to continue for a twenty-four-hour period to secure complete liberation of rare gases. (4) He + Ne and A + Kr + Xe were determined in the gas, using methods previously described by Cady and Cady.[2] Since spectroscopic tests showed that not more than traces of Ne, Kr or Xe could have been present in each case, the results of the analyses are reported in the table as helium and argon, respectively. (5) Potassium was determined in the mass resulting from the sodium carbonate fusion.

Conclusions: (1) These analyses indicate no regular increase of the A/K ratio with age. (2) The range in argon content is much less than that of helium. (3) Most of the argon in at least the first two samples probably originated from a source, perhaps the atmosphere, other than the

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[1] F. C. Thompson and S. Rowlands, *Nature*, **152**, 103 (1943).

[2] G. H. Cady and H. P. Cady, *Ind. Eng. Chem., Anal. Ed.*, **17**, 760 (1945).

TABLE I

COMPARISON OF AGE WITH THE RATIO A/K IN ROCKS

Description of sample	Location from which obtained	He, cc./g. at S. T. P.	A, cc./g. at S. T. P.	K, %	G. ats. A / G. ats. K	Approximate age in millions of years
Quartz, Cornucopia formation	Cornucopia, N. E. Oregon	0.022×10^{-4}	1.3×10^{-4}	0.027	8.4×10^{-4}	100 (Late Mesozoic)
Soda feldspar	Ohanepecosh Hot Springs, Washington	0.062×10^{-4}	1.9×10^{-4}	0.43	7.7×10^{-5}	30 (Tertiary)
Potash feldspar, Cornucopia formation	Cornucopia, N. E. Oregon	0.19×10^{-4}	3.25×10^{-4}	12.8	4.4×10^{-6}	100 (Late Mesozoic)
Bostonite	Marblehead, Massachusetts	$<0.005 \times 10^{-4}$	0.81×10^{-4}	2.08	6.8×10^{-6}	300 (Carboniferous)
Granite, Silver Plume Formation	Silver Plume, Colorado	2.4×10^{-4}	1.4×10^{-4}	1.91	1.3×10^{-5}	940[3]
Granite	Sudbury, Ont.	0.65×10^{-4}	4.5×10^{-4}	3.33	2.4×10^{-5}	700 (Keweenawan)
Granite gneiss	Sudbury, Ont.	0.51×10^{-4}	5.2×10^{-4}	1.05	8.6×10^{-5}	1050 (Laurentian)

decay of potassium-40 in the existing minerals. (4) A careful isotopic analysis would be required to establish the relative proportions of "atmospheric" argon and that formed by the decay of K^{40} in the rock. (5) Without such an analysis, the ratio, A/K, appears not to be a good measure of the age of a rock.[4]

(3) Age by U, Th, Pb method: E. N. Goddard and J. J. Glass, *Am. Mineralogist*, **21**, 199 (1936).

(4) Aldrich and Nier (*Phys. Rev.*, **74**, 876 (1948)) have reported since the date of submission of this note, that the ratio A^{40}/A^{36} is higher in potassium minerals than in air. Their analyses of four samples indicate an increase in the ratio Radio A/K with age.

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Some New Polyhalogenated Phenyl Isocyanates

BY LOUIS W. GEORGES[2] AND CARL HAMALAINEN

Previously reported work on the reaction of organic isocyanates with cellulose has been concerned with (1) the preparation of new cellulose derivatives of possible utility in the plastics field, and (2) the production of a more or less superficial esterification of cotton textiles to impart new properties. Thus, cellulose carbamate and cellulose acetate carbamate,[3] soluble in common organic solvents, and chlorophenyl carbamate of methyl cellulose with as much as 12% chlorine have been obtained.[4] By the preparation of carbamates, cotton textiles have been rendered water repellent,[5] their dyeing characteristics have been modified,[6] and the softening point and solubility properties of cellulose acetate rayon have been altered.[7]

The object of the present study was to investigate the possibility of providing a fire-resistant cotton textile by chemical combination of a fire-retarding agent with the cellulose molecule yet preserving the fibrous character of the cotton. Halogen-containing organic compounds are either not combustible or, in general, burn with difficulty. It seemed likely that partial carbamylation of cellulose with a polyhalogenated phenyl isocyanate would introduce sufficient halogen (27–31%) in cellulose to achieve fire-proofness and still retain the fiber structure. Such partial carbamylations could be successfully effected in a manner similar to that described by Hearon, Hiatt and Fordyce[3c] in which phenyl isocyanate was used. A patent covering the fireproofing of lint cotton has been issued.[8]

It is believed that the polyhalogenated phenyl isocyanates used in the reaction with cotton in the manner described in the patent are new compounds. The preparation of these compounds is given in the experimental section below.

Experimental

2,5-Dichlorophenyl Isocyanate.—Forty-five grams of 2,5-dichloroaniline hydrochloride was suspended in 500 ml. of chlorobenzene and phosgene[9] was passed through the suspension in a steady stream with stirring until complete solution of the hydrochloride was effected. During the

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Present address: Firestone Tire and Rubber Company, Akron, Ohio.

(3) (a) P. E. C. Goissedet, U. S. Patent 1,357,450 (November 2, 1920); (b) C. J. Malm and G. F. Nadeau, U. S. Patent 1,991,107 (February 12, 1935); (c) W. M. Hearon, G. D. Hiatt and C. R. Fordyce, THIS JOURNAL, **65**, 829 (1943); (d) W. M. Hearon and J. L. Lobsitz, *ibid.*, **70**, 296 (1948).

(4) E. Dyer and K. L. McCormick, *ibid.*, **68**, 986 (1946).

(5) (a) E. Schirm, U. S. Patent 2,303,364 (December 1, 1942); (b) W. Kaase, U. S. Patent 2,370,405 (February 27, 1945); (c) R. W. Maxwell, U. S. Patent 2,343,920 (March 14, 1944); (d) I. G. Farbenindustrie, A.-G., British Patent 461,179 (February 8, 1937); (e) British Patent 474,403 (November 1, 1937).

(6) P. S. Pinkney, U. S. Patent 2,350,188 (May 30, 1944).

(7) D. D. Coffman and J. S. Reese, British Patent 548,807 (December 25, 1942).

(8) L. W. Georges and C. Hamalainen, U. S. Patent 2,428,843 (October 14, 1947).

(9) (a) D. V. N. Hardy, *J. Chem. Soc.*, 2011 (1934); (b) J. Hilger, U. S. Patent 1,916,314 (July 4, 1933); (c) W. Hentrich and H. J. Engelbrecht, U. S. Patent 2,261,156 (November 4, 1941).