weight reported by Maas[6] requires a content of nine to eleven carbon atoms, and Lederer's suggestion that the eye pigments are pterine derivatives still appears to be a plausible one.[7]

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(6) W. Maas, *Genetics*, **33**, 177 (1948).

(7) We are indebted to Mrs. Evelyn Shirck McConnaughey for technical assistance in the culture of flies and in the preparation of the crude extracts.

DEPARTMENT OF CHEMISTRY AND DEPARTMENT OF BIOLOGY
UNIVERSITY OF OREGON
RECEIVED MAY 28, 1951

Densities in the Methanol–Water System at 25.00°

BY GERALDINE CLIFFORD AND J. A. CAMPBELL

Much work has been done on the methanol–water system but none of the vapor pressure data are sufficiently good to give a consistent check with the Duhem equation. The most convenient way to analyze solutions in this system is by means of density determinations. Since we find no data at 25.00° available (a convenient temperature for our purposes), we have determined the density–mole fraction relations for the system at 25.00° in order to undertake a complete study of the vapor–liquid equilibrium.

Experimental

The water used was distilled from acid dichromate solution and shown to be of conductivity grade. Reagent grade methanol was diluted with an equal volume of water and distilled from a ten-plate fractionating column to give a practically odorless methanol of density d^{25}_4 0.78687. "International Critical Tables" lists 0.78683.

Solutions of known composition were made by adding water to weighed ground glass stoppered bottles, weighing, adding methanol and weighing again. Each mole fraction should be accurate to within ±0.00002 unit.

Density determinations were made at each composition with two pycnometers, one of about 8 ml. volume, the other about 10 ml. calibrated with water as a standard. Every determined value of the density at each composition agreed with the values tabulated below to within ±0.00004. Deviations were independent of the pycnometer used.

Weights standardized against a Bureau of Standards calibrated set were used throughout and all values were corrected for the buoyancy of air.

The thermometer was standardized against a thermometer newly calibrated at the Bureau of Standards.

Results

The density of methanol–water solutions at 25.00° as a function of the mole fraction of methanol is given in Table I. No simple equation (third power or less) fits the data because of the high curvature at the ends of the composition range.

Mole fraction methanol (±0.00002)	d^{25}_4 (±0.00004)
0.00000	0.99707
.04998	.98225
.13479	.96202
.23820	.93912
.37528	.90852
.51984	.87733
.58901	.86306
.78902	.82386
.86674	.80968
1.00000	.78687

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RECEIVED JULY 6, 1951

Ultraviolet Absorption Spectra of N-Nitrocarbamates, N-Nitroamines and Salts of N-Nitroamines

BY HOWARD M. CURRY[1] WITH J. PHILIP MASON

Shortly after this study was begun, the ultraviolet absorption spectra of some compounds containing N-nitro and N-nitroso groups were reported by Carmack and Leavitt.[2] Since our program included the ultraviolet absorption spectra of N-nitrocarbamates and amine salts of N-nitroamines the investigation was continued. Recently, a comprehensive study of the ultraviolet absorption spectra of N-nitroso and N-nitro compounds has been reported by Jones and Thorn.[3] They did not include any data on N-nitrocarbamates or amine salts of N-nitroamines.

Seven N-nitrocarbamates have been investigated and found to exhibit absorption maxima in the range 235–240 mμ whereas the nitroamines and nitroamine salts have maxima in the range 232–235 mμ. The results for the nitroamines are consistent with those of Carmack and Leavitt[2] who observed maxima for their compounds in the region 228–236 mμ. These investigators used aqueous solutions.

TABLE I

Compound	$\lambda_{max.}$, mμ	$\epsilon_{max.}$
Ethyl N-nitro-N-isopropyl carbamate	240	4900
Ethyl N-nitro-N-*n*-propylcarbamate	239	6190
Methyl N-nitro-N-ethylcarbamate	235	6030
Ethyl N-nitro-N-ethylcarbamate	237	5630
n-Butyl N-nitro-N-*n*-butylcarbamate	238	6710
Ethyl N-nitro-N-*t*-butylcarbamate	239	2690
N,N′-Dinitro-N,N′-dicarbethoxy-1,6-diaminohexane	238	12070
Isopropyl-N-nitroamine	232	6810
Potassium salt of isopropyl N-nitroamine	234	8210
Isopropylamine salt of isopropyl-N-nitroamine	233	8200
Isobutylamine salt of cyclohexyl-N-nitroamine	235	8080

The results indicate that there is a slight shift toward the visible in the spectra of the N-nitrocarbamates although the shift is not of sufficient magnitude to serve as a means of distinguishing N-nitrocarbamates from N-nitroamines.

The intensities of absorption of the amine salts of N-nitroamines and of the one potassium salt which was measured were found to be consistently greater than the intensities of N-nitrocarbamates and N-nitroamines.

An appreciable decrease in intensity is noted in the N-nitrocarbamate series when the alkyl group attached to the nitrogen atom exhibits branching at the carbon atom adjacent to the nitrogen atom. This is exemplified in Table I for the two isomeric compounds ethyl N-nitro-N-*n*-propylcarbamate and ethyl N-nitro-N-isopropylcarbamate. Although the absorption maxima for these compounds fall in approximately the same position, the

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(1) Abstracted from a portion of the dissertation submitted by Howard M. Curry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) M. Carmack and J. J. Leavitt, THIS JOURNAL, **71**, 1221 (1949).

(3) R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B**, 828 (1949).

extinction coefficients at the maxima are seen to be 6190 and 4900, respectively. A much greater decrease in intensity is noted in the absorption maxima of *n*-butyl N-nitro-N-*n*-butylcarbamate and ethyl N-nitro-N-*t*-butylcarbamate which fall in the same position but the extinction coefficients at the maxima are seen to be 6710 and 2690, respectively. Although at present there is no theoretical treatment which will satisfactorily explain intensities, it is interesting to note that the intensity decrease is noted in the spectra of the only two compounds which could inhibit attainment of coplanarity in the N-nitro group and thus decrease the extent of its resonance.

The only dinitrodicarbamate which was measured, N,N′-dinitro-N,N′-dicarbethoxy-1,6-diaminohexane, exhibited an extinction coefficient of almost twice that of the mono nitro compounds, was expected since the ratio of N-nitro groups at any given concentration would be two to one.

All spectrophotometric measurements were made with 0.0001 *M* solutions in specially purified ethyl alcohol,[4] in 1-cm. quartz cells in a Beckman quartz spectrophotometer, model DU. The results are summarized in Table I.

(4) A. Castille and V. Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

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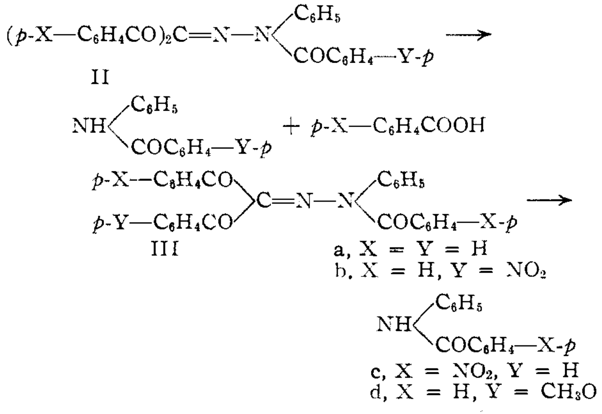
RECEIVED JANUARY 23, 1951

The N,N-Cleavage of Benzoylphenylhydrazones by Bases[1]

BY DAVID Y. CURTIN[2] AND CHARLOTTE SANANES RUSSELL

During the course of the work described in the preceding paper[3] an attempt was made to separate a mixture of the two hydrazones, IId and IIId, by chromatography on alumina. It was found, however, that when the hydrazones were adsorbed on the column from benzene and eluted with benzene containing 10% ethanol the only products obtained were benzanilide and anisanilide in estimated yields of 52 and 33%.


II

III

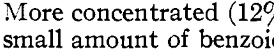
a, X = Y = H
b, X = H, Y = NO$_2$
c, X = NO$_2$, Y = H
d, X = H, Y = CH$_3$O

Further investigation showed that diphenyltriketone benzoylphenylhydrazone (IIa) gave a 60% yield of benzanilide. Not only was this reaction of interest in its own right but it provided a means of establishing the structures of the nitro-substituted diphenyltriketone benzoylphenylhydrazones (IIIb, IIc and IIIc) obtained in the previous paper[2] since their method of formation gave no basis for distinguishing between the isomeric formulas, II and III.

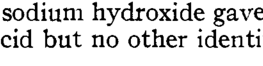
The structure of the hydrazone which had been designated as *p*-nitrophenyl phenyltriketone (IIIb) was established by its conversion to benzanilide in 75% yield by chromatography on alumina. Similarly the structure of *p*-nitrophenyl phenyltriketone *p*-nitrobenzoylhydrazone (IIIc) was assigned on the basis of its cleavage to *p*-nitrobenzanilide in 64% yield.

It has been found, moreover, that the N,N-cleavage can be effected with dilute boiling sodium hydroxide solution. IIIb, when treated with boiling 0.5% sodium hydroxide solution, gave benzanilide in 60% yield together with a mixture of benzoic and *p*-nitrobenzoic acid. Although IIIc had reacted smoothly on alumina, treatment with sodium hydroxide failed to convert it to isolable products. Bis-*p*-nitrophenyl triketone benzoylphenylhydrazone (IIc) reacted readily with dilute sodium hydroxide to give a 74% yield of benzanilide and 70% of *p*-nitrobenzoic acid.

In an attempt to extend this reaction, benzophenone *p*-nitrobenzoylphenylhydrazone (IV) was prepared and its behavior toward base studied. Twelve hours of refluxing with 5% sodium carbonate did not alter IV. Absorption of IV on alumina and elution with benzene–ethanol yielded 26% of benzophenone phenylhydrazone and 74% recovered IV. Dilute hydrochloric acid converted IV to benzophenone and α-*p*-nitrobenzoylphenylhydrazine.


$(C_6H_5)_2C{=}NN(C_6H_5)(COC_6H_4NO_2)$

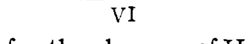
IV


$(C_6H_5)(C_6H_5CO)C{=}NN(C_6H_5)(COC_6H_5)$

V

Benzoin benzoylphenylhydrazone (V) was also examined. V could be recovered unchanged after chromatography on alumina but when allowed to stand adsorbed on the column for nine days and then eluted, a 67% yield of benzil phenylhydrazone was the only neutral product isolated. V was unchanged by refluxing 1% sodium hydroxide. More concentrated (12%) sodium hydroxide gave a small amount of benzoic acid but no other identifiable product.

An N,N-cleavage of acylphenylhydrazones appears to have been observed previously in only one case. Auwers and Eisenlohr[4] found *p*-quinone benzoylphenylhydrazone (VI) to be converted on treatment with 1% aqueous sodium hydroxide to benzanilide (in yields up to 75%), together with *p*-aminophenol (small amounts), benzoic acid, *p*-hydroxyazobenzene and ammonia.


VI

Mechanisms for the cleavage of II may be formulated with initial attack of hydroxyl ion at either carbon or nitrogen. Attempts to distinguish

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(1) Abstracted from a thesis presented by Mrs. C. S. Russell in partial fulfillment of the requirements for the Ph.D. Degree at Columbia University.

(2) Department of Chemistry, University of Illinois, Urbana, Ill.

(3) D. Y. Curtin and C. S. Russell, THIS JOURNAL, **73**, 5160 (1951).

(4) K. Auwers and F. Eisenlohr, *Ann.*, **369**, 209 (1909).