TABLE I

ESTIMATION OF STANDARD ENTROPIES[a] $S^0_{298(g)}$

	σ	X = H S^0(obsd.)	Y = F S^0(calcd.)	X = H S^0(obsd.)	Y = Cl S^0(calcd.)	X = H S^0(obsd.)	Y = Br S^0(calcd.)	X = F S^0(obsd.)	Y = Cl S^0(calcd.)
CX_4	12	44.50	...	44.50	...	44.50	...	62.7	...
CX_3Y	3	53.30	53.43	55.97	56.23	58.74	59.14	...	69.89
CX_2Y_2	2	...	58.17	64.68	63.80	70.16	69.62	...	72.90
CXY_3	3	...	62.53	70.86	70.95	79.18	79.68	74.06	75.51
CY_4	12	62.7	...	73.95	...	85.6	...	73.95	...

[a] All of the observed entropy values were taken from the National Bureau of Standards, Circular 500, Washington, D. C., 1952.

tional contributions when added together become an approximately linear function of the composition of the compound. The rotational entropy contribution, however, deviates considerably from linearity since it depends on the symmetry number σ, of the various molecules. The symmetry number arises through the term $- R \ln \sigma$ in the equations for the evaluation of the rotational entropy by statistical thermodynamics.

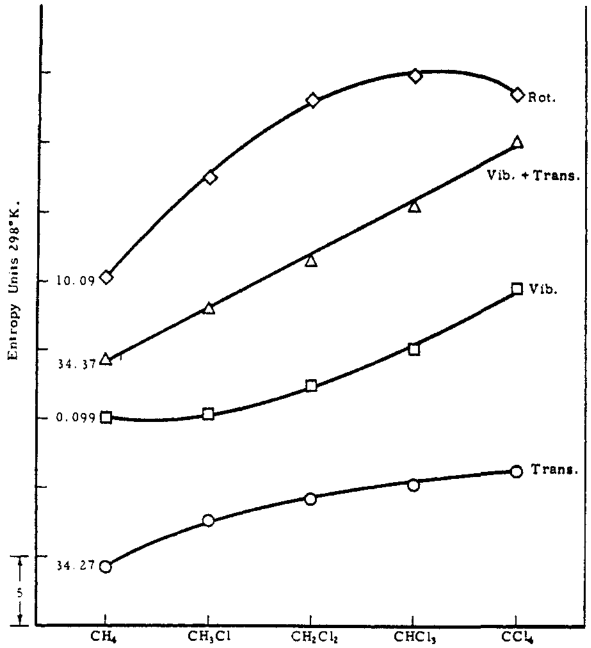

Fig. 1.—Contributions to the standard entropy S°_{298}(g).

Consequently, linear interpolation of $S^0(g) + R \ln \sigma$ leads to satisfactory agreement with observed values for the type of series herein considered (Table I). The average deviation between observed and calculated values for the compounds in Table I is 0.5 entropy unit.

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Distribution of 8-Quinolinol between Water and Chloroform as a Function of *p*H

BY THERALD MOELLER AND FRED L. PUNDSACK

RECEIVED DECEMBER 20, 1952

The extensive use of 8-quinolinol as an analytical reagent is dependent upon its ability to form with many metal ions water-insoluble chelates which are applicable to both gravimetric and colorimetric determinations. For determinations of the latter type, a number of procedures based upon extraction of metal ions from aqueous solutions into chloroform solutions of 8-quinolinol and subsequent spectrophotometric examinations of the extracts have been proposed.[1-6] These extractions are dependent upon the *p*H of the aqueous phase, and their usefulness is limited somewhat by the concentration of free 8-quinolinol in the chloroform phase, a large excess of free 8-quinolinol interfering markedly with spectrophotometric determinations of the metal chelate concentrations. Inasmuch as the quantity of 8-quinolinol in the chloroform phase is itself *p*H dependent, it would help in establishing optimum conditions for quantitative extraction of metal chelates to evaluate the distribution of the reagent between water and chloroform as a function of *p*H.

From concentration measurements at 18°, Lacroix[2] has calculated a distribution coefficient

$$c_{CHCl_3}/c_{H_2O} = 720 \qquad (1)$$

for molecular 8-quinolinol. In addition, he has evaluated a theoretical distribution curve, based upon data for two extractions, which shows extraction into chloroform to be complete in the *p*H range *ca.* 4–11, but has offered only limited experimental support. No equilibrium studies on this distribution appear to have been made.

Experimental

Reagents.—The 8-quinolinol was an Eastman Kodak Co. product which had been recrystallized from ethanol. Other chemicals were of reagent quality.

Apparatus.—Spectrophotometric measurements were made with a Beckman model DU spectrophotometer. A Beckman model G *p*H meter, the glass electrodes of which were calibrated frequently against suitable buffers, was used for all *p*H measurements.

Procedure.—Twenty-five ml. portions of a chloroform solution of accurately known 8-quinolinol concentration were agitated with 25-ml. volumes of aqueous solutions of known *p*H values in a constant temperature bath at 25.0 ± 0.1°. The concentration of the original chloroform solution was determined spectrophotometrically, using the 3154 Å. absorption peak of 8-quinolinol in this solvent.[7] The *p*H of the aqueous phase was adjusted by using sulfuric acid, sodium acetate and sodium hydroxide as required.

Contact between aqueous and chloroform phases for 24 hours was shown to be sufficient to ensure complete concentration equilibration. After a 24-hour contact period in each instance, the total 8-quinolinol content of the aqueous phase was determined spectrophotometrically on an aliquot, using the light absorption at 2505 Å. for acidic solu-

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[1] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943).

[2] S. Lacroix, *Anal. Chim. Acta*, **1**, 260 (1947).

[3] T. D. Parks and L. Lykken, *Anal. Chem.*, **20**, 1102 (1948).

[4] C. H. R. Gentry and L. G. Sherrington, *Analyst*, **75**, 17 (1950).

[5] T. Moeller and A. J. Cohen, *Anal. Chem.*, **22**, 686 (1950).

[6] J. L. Kassner and M. A. Ozier, *ibid.*, **23**, 1453 (1951).

[7] F. L. Pundsack, Doctoral Dissertation, University of Illinois (1952).

tions and that at 2525 Å. for alkaline solutions.[7] Neutral and nearly neutral solutions were acidified with sulfuric acid and the absorption determined at 2505 Å. Concentration of residual 8-quinolinol in the chloroform phase was determined by difference in each case. The distribution coefficient was then evaluated as the ratio of the molar concentration of 8-quinolinol in the chloroform phase to the total molar concentration of all 8-quinolinol species in the aqueous phase. Substitution of concentrations for activities was permissible because of the low concentration levels employed.

Discussion

Variation in distribution coefficients with *p*H, as indicated in Table I, are easily understood in terms of the amphoteric character of 8-quinolinol. The basic and acidic properties of the compound are described by the equilibria

TABLE I

DISTRIBUTION OF 8-QUINOLINOL BETWEEN CHLOROFORM AND WATER AT 25°

*p*H	Σc_{H_2O}[a] mole/liter, × 10^5	c_{CHCl_3}[b] mole/liter, × 10^3	c_{CHCl_3}/c_{H_2O}	Molecular HOn in aqueous layer, %
2.06	9.90	0.0575	0.58	0.12
2.65	4.28	0.0792	1.85	0.44
3.75	4.40	1.17	26.4	5.32
4.43	1.51	1.36	89.9	21.2
6.05	0.489	1.72	352	92
7.00	.351	1.21	350	99
7.05	.475	1.71	360	99
8.21	.489	1.72	352	98
9.24	.055	0.121	221	80.5
10.50	2.06	1.36	65.8	18.4
12.00	4.82	0.105	2.18	0.71

[a] Sum of concentrations of molecular, cationic and anionic species. [b] Concentration of molecular species.

$$\text{HOn} + \text{H}^+ \rightleftarrows \text{HOn}\cdot\text{H}^+ \qquad (2)$$

$$\text{HOn} \rightleftarrows \text{H}^+ + \text{On}^- \qquad (3)$$

where HOn represents molecular 8-quinolinol. The basic and acidic dissociation constants have been determined[2,8–10] and permit evaluation of the concentrations of all three species at any *p*H. Since the only species existent in chloroform is the molecular one, it follows that essentially complete concentration of 8-quinolinol in the chloroform phase can be expected only over that *p*H range in which the quantity of the molecular species is maximum in the aqueous phase. As shown in Table I, *ca.* 99% of the 8-quinolinol in the latter phase is in the molecular form in the *p*H range 7.0–8.2, with more than 90% being molecular at as low a *p*H as 6.0. In this *p*H range, the average experimental distribution coefficient of 353 closely approximates that calculated for molecular 8-quinolinol.

On the other hand, in either more acidic or more alkaline aqueous solutions, only a small fraction of the 8-quinolinol present is in the molecular form. The experimentally determined distribution coefficients, as based upon the total 8-quinolinol concentration in the aqueous phase, decrease correspondingly. Thus, although the distribution coefficients given in Table I are really theoretical values for only the 6.0–8.2 *p*H range, they are of practical importance in determining optimum *p*H conditions for 8-quinolinol extractions.

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(8) K. Stone and L. Friedman, THIS JOURNAL, **69**, 209 (1947).

(9) J. P. Phillips and L. L. Merritt, *ibid.*, **70**, 410 (1948).

(10) H. Irving, J. A. D. Ewart and J. T. Wilson, *J. Chem. Soc.*, **2672** (1949).

Isolation of Methylchrysene from Petroleum

BY R. J. MOORE, R. E. THORPE AND C. L. MAHONEY

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In the course of examining a Mid-continent medium petroleum distillate by silica gel chromatography, a white crystalline material has been isolated which is identified as 1-methylchrysene. After recrystallization from ethanol, the melting point was 253° (compared with 251° found by Brode and Pattersen[1]). The ultraviolet absorption spectrum was identical to that reported for synthetic 1-methylchrysene and the parent mass found with a high temperature mass spectrometer was 242, corresponding to $C_{19}H_{14}$. Excepting the *n*-paraffins, we believe that this is the highest molecular weight pure hydrocarbon thus far isolated from native petroleum.

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(1) W. R. Brode and J. W. Pattersen, THIS JOURNAL, **63**, 3252 (1941).

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Carbazic Acid Esters as Carbonyl Reagents

BY NORMAN RABJOHN AND H. D. BARNSTORFF[1]

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The common derivatives of aldehydes and ketones such as phenylhydrazones, substituted phenylhydrazones, oximes and semicarbazones, as well as a rather large number of lesser known condensation products, are described extensively in the literature and textbooks for qualitative organic analysis. However, it appears that little use[2] has been made of the esters of carbazic acid as carbonyl reagents. These materials are stable, crystalline solids which can be synthesized readily from hydrazine and an organic carbonate.

The present work describes the preparation of a number of carbonyl derivatives of methyl and ethyl carbazates which have not been reported previously. The data obtained for a series of carbomethoxyhydrazones are given in Table I. The properties of the carboethoxyhydrazones are listed in Table II.

Formaldehyde, benzalacetophenone and benzil gave mixtures of products with both methyl and

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(1) From a thesis submitted by Henry D. Barnstorff to the Graduate School of the University of Missouri, 1949, in partial fulfillment of the requirements for the degree of Master of Arts.

(2) A relatively few derivatives are recorded in the following leading references: K. v. Auwers and Th. Breyhan, *J. prakt. Chem.*, **143**, 259 (1935); H. J. Backer and W. Meyer, *Rec. trav. chim.*, **45**, 82 (1926); H. DeGraff, Diss. Leiden (1930), *C. A.*, **24**, 5723 (1930); O. Diels and P. Fritzsche, *Ber.*, **44**, 3018 (1911); D. N. Majumdar and P. C. Guha, *J. Indian Chem. Soc.*, **10**, 685 (1933); and R. B. Woodward, T. P. Kohman and G. C. Harris, THIS JOURNAL, **63**, 120 (1941).