gas oils has been reported (*1*). Their concentration probably never exceeds 1 to 2% weight, and could be corrected for by an independent determination of total oxygen (as in the case of nitrogen compounds). The standard deviation of this method is estimated at ±1 to 2% weight for each class reported, on the basis of multiple determination for several of the samples of Table IV. Linearity in the routine separation was checked for several samples; the recommended sample sizes are less than half the amount necessary to produce appreciable dependence of the analysis results on sample size.

The peculiar distribution of aromatic type *vs.* boiling point in catalytically cracked samples has been noted by many workers in the past, and arises from the tendency of aromatic and olefinic components to be stripped of alkyl substituents down to a nucleus plus 1 to 4 alkyl carbon atoms. As a result, olefins concentrate in the C_3 to C_5 range, monoaromatics predominate in the gasoline fraction, and the higher aromatic types are distributed as in Figure 7.

The present method is not directly applicable to straight-run or related sample types, and may be inapplicable in principle to such samples. Absorptivity data for various diaromatic fractions isolated from straight-run sample types show considerable variability, (even after correction for alkyl sulfide content) and are generally substantially lower than values for corresponding cracked samples. This is believed to reflect the presence in straight-run samples of significant, but variable, amounts of the diphenylalkanes, compounds that separate with the diaromatics and exhibit much lower absorptivities at 230 mμ. The diphenylalkanes would be expected to crack to gasoline-range benzenes, leaving little of this compound type in cracked gas oils. On the basis of preliminary data, the determination of monoaromatics in straight-run samples by the procedure described appears to give erroneously high results, for as yet undiscovered reasons. It is clear that a number of problems exist in the extension of this type of analysis to include straight-run sample types.

ACKNOWLEDGMENT

The author thanks F. O. Wood and A. E. Youngman of this laboratory for assistance in the experimental work.

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RECEIVED for review October 21, 1963. Accepted January 10, 1964.

Spectrophotometric Titration of Primary Aliphatic Amides

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▶ A spectrophotometric titration method has been developed for the determination of primary aliphatic amides. The titration is carried out in an aqueous bromide solution, buffered at pH 10 with a standard solution of calcium hypochlorite. The end point is determined from the ultraviolet absorbance of the excess hypobromite.

BECAUSE of the nonreactive nature of the amide functional group, most of the available analytical procedures for amides are difficult and time-consuming. For example, saponification procedures for amides require at a minimum 30 minutes reaction time (*6*), and procedures based upon conversion to hydroxamic acids require a 1- to 6-hour reaction time (*1*, *7*). The lithium aluminum hydride method (*8*), although relatively specific, requires a steam distillation step after a 15-minute reaction period and the procedure cannot be used for dilute aqueous solutions of amides. Nonaqueous acid-base methods (*3*, *9*) are not specific for amides, since many other weakly basic substances interfere. Probably the most generally applicable method for primary amides is that developed by Mitchell and Ashby (*5*) which utilizes 3,5-dinitrobenzoyl chloride as a reagent, but even this procedure requires a reaction time of from 30 minutes to 1 hour and also requires a blank titration for every sample.

In the present work the first reaction step in the familiar Hofmann rearrangement of an amide to an amine has adapted to a spectrophotometric titration procedure for primary aliphatic amides. A sample of amide is dissolved in an aqueous solution which is 0.1*M* in potassium bromide and which is strongly buffered at pH 10 with borax. The solution is titrated with a standard solution of calcium hypochlorite, and the hypobromite ion produced in situ immediately reacts with amide to form the *N*-bromoamide. The titration is followed by observing the absorbance of hypobromite at 350 mμ. A complete titration can be finished in 5 to 10 minutes.

EXPERIMENTAL

Reagent and Apparatus. An approximately 0.1*N* solution of calcium hypochlorite was prepared by dissolving reagent grade calcium hypochlorite in water, followed by filtration to remove solid calcium carbonate. The solution was standardized iodometrically. The titer of this standard solution decreased approximately 0.2% per week.

A borax buffer solution was prepared by adding a concentrated, carbonate-free, sodium hydroxide solution to a saturated solution of sodium tetraborate until a pH of 10.0 was reached.

Most of the amides used were of the highest purity obtainable from commercial sources and were used without