Irradiation of 1,3-Dinitrobenzene.—1,3-Dinitrobenzene (10 g.) was placed in 500 ml. of absolute ethanol and irradiated for 72 hr. Filtration of the resultant suspension afforded 3.20 g. of starting material. Evaporation of the solvent left 6.80 g. of crude brown material, m.p. 45–70°. Two grams of this crude material was chromatographed on alumina. Starting material, 1.25 g., eluted off in petroleum ether. In 1:5 petroleum ether-benzene eluent, 0.104 g. (2.7%) of crystals was found of m.p. 140–143°; mixture melting point of an authentic sample of 3,3′-dinitroazoxybenzene was 138–142°. The ultraviolet and infrared spectra were identical.

Formic Ethylcarbonic Anhydride[1]

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The preparation of a number of stable mixed carboxylic carbonic anhydrides,[2] RCOOCOOR′ (R = aryl or alkyl and R′ = alkyl) has prompted us to study the synthesis and properties of formic ethylcarbonic anhydride (A). The symmetrical anhydride of formic acid is unstable[3]; the mixed anhydride of formic and acetic acid is well known,[4] however, and has been used to acylate on oxygen and nitrogen. Formyl chloride, HCOCl, appears to be stable for a few hours[5] at −60°, and formyl fluoride is readily accessible.[3,6]

Treatment of carefully dried formic acid with ethyl chlorocarbonate and triethylamine in ether at −15° for 15–20 min. gave a nearly quantitative yield of triethylamine hydrochloride; the filtrate, after shaking with solid sodium bicarbonate, showed strong bands in the infrared at 1730 and 1793 cm.$^{-1}$, indicative of the presence of mixed carboxylic–carbonic anhydride.[2] Dimethyl ether was also used as solvent in some runs.

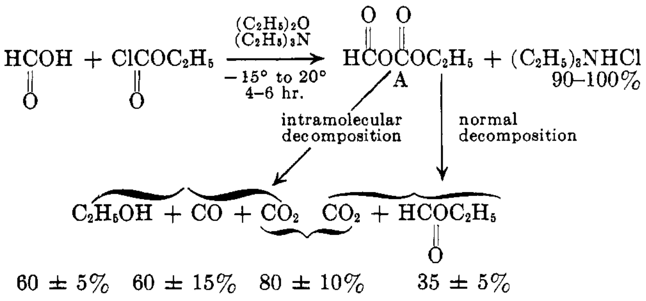
The presence of the mixed anhydride was verified by preparation of the formyl derivative of α-naphthylamine; the latter was added to ethyl chlorocarbonate in ether at 15°, 15 min. after triethylamine was added. The mixture was stirred for 30 min. and the formyl-α-naphthylamine obtained was identical with a known sample.[7]

The residue from the filtrate prepared as above gave a mixture which was shown by v.p.c. analysis and n.m.r. measurements to consist of ethyl alcohol and ethyl formate. Quantitative analyses for ethanol and ethyl formate showed that, in about ten runs, the average yields were 60 ± 5% of alcohol and 35 ± 5% of ester. The triethylamine hydrochloride was obtained in 90–100% yield.

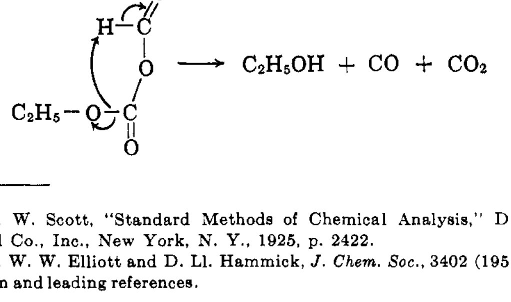
The appearance of ethyl formate can be readily explained by the formation of the mixed anhydride A, which then lost carbon dioxide to form the ester, analogous to other mixed anhydrides, which, however, require temperatures much higher than 0° to decompose in this manner. The formation of carbon dioxide was verified and followed by sweeping the reaction mixture with nitrogen and collecting the carbon dioxide in weighed ascarite tubes. The yields of carbon dioxide were 80 ± 10%, based on complete reaction of the formic acid. It was also observed that 20% of the carbon dioxide was evolved in the first hour and the decomposition was almost complete in 4–6 hr. after the reactants were mixed; the temperature ranged from −15° in the beginning of the reaction to room temperature at the end. Along with the observation from titration experiments that disappearance of formic acid was almost complete 1 hr. after the reactants were mixed, this proved that the mixed anhydride is stable for a short time in that temperature range.

The formation of ethyl alcohol was unexpected; no evidence for the presence of diethyl carbonate could be obtained, but carbon monoxide was shown to be formed by absorbing the gases swept by nitrogen from the reaction mixture of formic acid, ethyl chlorocarbonate, and triethylamine. The carbon monoxide was quantitatively absorbed in a series of bulbs containing cuprous sulfate in sulfuric acid[8] and the yield was 60 ± 15% in about ten runs.

The mixed anhydride appears to decompose by two routes, indicated below, and the yields are in agreement with this.



The decarbonylation of formic acid derivatives[9] is well known, but normally requires more drastic conditions than those prevailing here: solution in ether in essentially neutral solution at 0°. The decomposition of the mixed anhydride to form carbon monoxide, carbon dioxide, and ethanol may involve the following process which may be promoted by traces of catalysts (chloride ion, triethylamine, or protons, depending on circumstances) in the reaction mixture.



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[1] Supported by Grant G-11240 from the National Science Foundation.

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[9] *Cf.* W. W. Elliott and D. Ll. Hammick, *J. Chem. Soc.*, 3402 (1951), for discussion and leading references.

Experimental

Formation of Formic Ethylcarbonic Anhydride.—Formic acid (99+%) prepared using phthalic anhydride[10] (4.6 g., 0.1 mole) was dissolved in 200 ml. of anhydrous ether, and freshly distilled ethyl chlorocarbonate (10.9 g., 0.1 mole) was added and the mixture was cooled to −15°. Freshly distilled triethylamine (10.1 g., 0.1 mole) was added dropwise with stirring, preventing rise in temperature. At the end of 30 min., a portion of this mixture was quickly shaken with solid sodium bicarbonate, the mixture was filtered, and the infrared spectrum was taken in the ether solution; it revealed peaks at 1730 and 1793 cm.$^{-1}$, indicating the formation of the expected mixed anhydride, but attempts to isolate it ended in failure.

Evidence for the Existence of the Mixed Anhydride.—The preparation of the mixed anhydride was done exactly as outlined above except that 15 min. after the reaction mixture had been stirred at −15°, α-naphthylamine (14.3 g., 0.1 mole) in ether was added to the mixture and stirring continued for 1 hr. The mixture was then filtered and the pale pink ether solution was washed with dilute acid, saturated bicarbonate solution, and several times with water. The ether solution was evaporated to dryness, giving 6 g. of a crude product which after two or three recrystallizations from benzene melted at 142°. This product did not depress the melting point of the formyl-α-naphthylamide, m.p. 142°, prepared from formic acid and α-naphthylamine independently. The infrared spectra of both samples were identical.

Determination of Carbon Dioxide and Carbon Monoxide.—In a three-necked flask fitted with an addition flask, a gas inlet tube, and a Dry Ice condenser, were placed formic acid (4.6 g., 0.1 mole) and ethyl chlorocarbonate (10.9 g., 0.1 mole) in 200 ml. of anhydrous ether. A gentle stream of nitrogen was passed through an ascarite bulb into the flask. Two previously weighed ascarite bulbs followed by three weighed bulbs containing freshly prepared cuprous sulfate in sulfuric acid[8] were connected to the exit outlet of the Dry Ice condenser. While the ether was cooled at −15°, triethylamine (10.1 g., 0.1 mole) was added dropwise with stirring. Stirring was continued for 2 hr. at −15 to 0° and the temperature was allowed to rise to room temperature at the end of 4–6 hr. While the stream of nitrogen was continued care was taken to replenish the Dry Ice condenser with Dry Ice and acetone to condense any ether that might be carried by the nitrogen. The ascarite and cuprous sulfate bulbs were weighed at various time intervals and usually there was no increase in weight after 4–6 hr. The yields of CO_2 and CO are based on values obtained from about ten runs and were 80 ± 10% and 60 ± 15%, respectively.

Estimation of Ethanol and Ethyl Formate.[11,12]—In the above reaction after the completion of the evolution of the carbon dioxide and carbon monoxide, the mixture was filtered into a volumetric flask and the volume was made up to 250 ml. by washing the amine hydrochloride several times with dry ether. The ethanol was estimated by taking accurately 25 ml. of this solution and treating with acetic anhydride and pyridine on a steam bath for 2 hr. and titrating the excess acetic acid with standard alkali.[12] The ester in the mixture was determined by standard saponification procedures.[12] The average values of eight to ten runs ran parallel to the estimation of these components in the v.p.c. method.[11] Pure ethanol (0.1 μl.), ethyl formate, and ether were run through an Apiezon L column at 55° and also an Ucon Polar column at 75° in the Hy-Fi Aerograph which is equipped with an integrator and a hydrogen flame ionization detector. The areas were considered proportional to the integral values and thus calibrations were made for the pure substances. Several runs of the unknown mixture (0.1 μl.) were run through the columns and from the integral values the yield of ethanol was found to be 60 ± 5%, based on complete reaction between formic acid and ethyl chlorocarbonate, and that of ethyl formate was 35 ± 5% on the same basis.

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A Convenient Preparation of 1-Diazopropane

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A simple method for the preparation of 1-diazopropane was required. An examination of the literature revealed that 1-diazopropane has been prepared from N-nitroso-N-*n*-propylurethan (57%),[1] N-nitroso-β-*n*-propylaminoisobutyl methyl ketone (44%),[2] N,N′-dinitroso-N,N′-di-*n*-propyloxamide (50%),[3] and 1-*n*-propyl-1-nitroso-3-nitroguanidine (55%).[4] The preparation of a number of N-nitroso-N-alkylureas and their conversions into diazoalkanes has been reported.[5] This procedure has not been used for the preparation of N-nitroso-N-*n*-propylurea and its conversion into 1-diazopropane. As the latter procedure would appear to be shorter and less hazardous than the others, we undertook its investigation. The results supplement the existing methods.

N-Nitroso-N-*n*-propylurea was prepared in 30% yield by nitrosation of N-*n*-propylurea and in 28% over-all yield from butyramide through N-*n*-propyl-N′-*n*-butyrylurea. The product was stable at room temperature for at least a month and at refrigerator temperature for over 3 years as evidenced by the absence of any change in the melting point, infrared spectrum, or yield of 1-diazopropane obtained. The urea was converted in 52% yield to 1-diazopropane using the procedure[6] for the small-scale preparation of diazomethane from N-nitroso-N-methylurea. The product obtained from 1-diazopropane and benzoic acid was shown to be exclusively *n*-propyl benzoate by n.m.r. spectroscopy.

Nitrosation of N-isopropylurea, in an attempt to prepare N-nitroso-N-isopropylurea, and hence 2-diazopropane by this method, resulted even at −15° in a brisk evolution of colorless gases. This observation is in accord with the reported[7] instability of 2-diazopropane.

Experimental[8]

N-Nitroso-N-*n*-propylurea. A. From N-*n*-Propylurea.—A solution of 88.5 g. (1.50 moles) of *n*-propylamine in 250 ml. of water was cooled in an ice–acetone bath and neutralized (methyl red) by the addition of 127 ml. of concentrated hydrochloric acid. Urea (300 g., 5.0 moles) was added to the solution and the solution was boiled under reflux for 3 hr. Sodium nitrite (110 g., 1.60 moles) was dissolved in the solution, which was then cooled in an ice–acetone bath and siphoned, during 1 hr., under the surface of a stirred mixture of 100 g. of concentrated sulfuric acid and 600 g. of ice, which was also cooled by an ice–acetone

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[8] Melting points were observed using a Kofler hot stage and are corrected. Infrared spectra were obtained using a Perkin-Elmer Model 137 Infracord instrument. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.