CXXXV.—*The Action of Nitric Acid on Acetylene and Ethylene.*
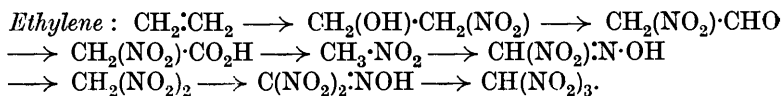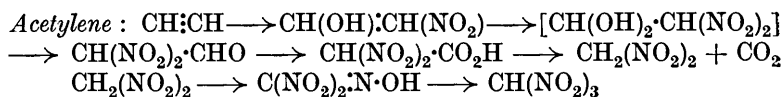
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IT has been shown (Orton and McKie, J., 1920, **117**, 283) that the principal products of the interaction of fuming nitric acid with acetylene are carbon dioxide and trinitromethane. In the reaction between fuming nitric acid and ethylene a similar formation occurs, but prior to the production of trinitromethane the addition compound, β-nitroethyl alcohol, is formed.

It is now possible to formulate a course of reaction between nitric acid and an ethylenic or acetylenic compound. From the presence in the products of (*a*) β-nitroethyl alcohol (from ethylene)

and (*b*) nitrolic acids, and the direct formation of nitroparaffins from these compounds, it is deduced that the primary reaction is one of addition of hydroxyl and the nitro-group to the unsaturated linking, forming the nitro-alcohol. This, in the case of acetylene, becomes by further addition the unstable dinitrodihydroxy-compound. Oxidation and reaction with nitrous acid gives the corresponding nitrolic acid, together with carbon dioxide, from which trinitro-methane is finally derived. Such a reaction is entirely in harmony with the reaction between oxides of nitrogen and unsaturated linkings (Schmidt, *Ber.*, 1901, **34**, 3536; 1902, **35**, 2323) and with the addition of nitric acid to various unsaturated compounds (Wieland and Rahn, *Ber.*, 1921, **54**, 1770; Cohn, *Ber.*, 1891, **24**, 3865).

The following equations represent the probable courses of reaction :

Acetylene : $CH:CH \longrightarrow CH(OH):CH(NO_2) \longrightarrow [CH(OH)_2 \cdot CH(NO_2)_2]$
$\longrightarrow CH(NO_2)_2 \cdot CHO \longrightarrow CH(NO_2)_2 \cdot CO_2H \longrightarrow CH_2(NO_2)_2 + CO_2$
$CH_2(NO_2)_2 \longrightarrow C(NO_2)_2 : N \cdot OH \longrightarrow CH(NO_2)_3$

Ethylene : $CH_2:CH_2 \longrightarrow CH_2(OH) \cdot CH_2(NO_2) \longrightarrow CH_2(NO_2) \cdot CHO$
$\longrightarrow CH_2(NO_2) \cdot CO_2H \longrightarrow CH_3 \cdot NO_2 \longrightarrow CH(NO_2) : N \cdot OH$
$\longrightarrow CH_2(NO_2)_2 \longrightarrow C(NO_2)_2 : NOH \longrightarrow CH(NO_2)_3.$

EXPERIMENTAL.

Dry ethylene (97—99% purity), prepared by the vaporisation of ethyl alcohol in an iron combustion tube packed with pumice stone soaked in syrupy phosphoric acid and heated to 250—300°, was passed into fuming nitric acid diluted to various concentrations. The experimental procedure was in all respects similar to that used for acetylene (Orton and McKie, *loc. cit.*). The absorption of ethylene by concentrated nitric acid is rather less ready than is that of acetylene, and there is a markedly lower evolution of carbon dioxide. The ratio Carbon dioxide evolved/Ethylene absorbed is, for 95% nitric acid, 0·4 : 1; whereas the ratio Carbon dioxide evolved/Acetylene absorbed is 0·8 : 1; in the presence of mercury salts, however, these ratios show a closer approximation. The yield of tetranitromethane obtained by further nitration of the product (Orton and McKie, *loc. cit.*), expressed as a percentage of the hydrocarbon absorbed, in the ethylene reaction never rises to, and is often much less than, the value obtained for acetylene, and no variation of experimental conditions has altered this relation. The maximum yield of tetranitromethane in one operation in the absence of a catalyst is obtained by the absorption of 2·7—2·9 l. of acetylene or of 2·9—3·1 l. of ethylene by 100 g. of 95% nitric acid. The yield of tetranitromethane is 9—10 g. (from acetylene),

or 277% of the acetylene absorbed, or 6—7 g. (from ethylene), or
231%.   The addition of 0·66% of mercuric nitrate raises the value
for ethylene to 332·9% (compare acetylene, 453—532%).   Hence
the amount of carbon in the ethylene reaction used up in side
reactions is considerable, 30—40%, which can partly be accounted
for by the formation of oxalic acid representing 28%.

TABLE I.

% HNO_3.	Per 100 g. of HNO_3.		$C(NO_2)_4$ as percentage of C_2H_4 absorbed.	% C in C_2H_4 becoming		
	C_2H_4 (l.) absorbed.	CO_2 (l.) evolved.		$C(NO_2)_4$.	CO_2.	other substances.
100	2·146	——	98·4			
97·5	3·100	——	116·2			
95·0	2·980	——	231·8			
95·0	2·764	2·504	204·3			
90·0	2·980	0·210	198·1			
90·0	2·846	0·451	201·4			

Compare acetylene :

95·0	2·288	2·855	278·7			

0·33% Mercuric nitrate as catalyst.

95·0	2·900	1·930	300·4	21·46	37·98	40·56

0·66% Mercuric nitrate as catalyst.

95·0	3·044	2·453	332·9	23·78	40·3	35·92

Compare acetylene :

95·0	3·02	4·39	383·0	29·2	70·8	0·0

TABLE II.

Relation between oxalic acid produced and hydrocarbon absorbed.

% HNO_3.	Hydro- carbon absorbed (l.).	CO_2 evolved (l.).	$H_2C_2O_4$ (g.).	$\dfrac{CO_2}{H_2C_2O_4}$ by wt.	% C becoming			Carbon unac- counted for.
					CO_2.	$C(NO_2)_4$.	$H_2C_2O_4$.	
Ethylene :								
95	3·152	2·699	2·774	1·93	42·5	25·34	21·61	10·55
90	1·484	0·608	1·710	0·71	20·49	29·8	28·34	21·37
Acetylene :								
95	3·792	3·212	2·357	2·69	42·15	17·42	15·29	25·14

Influence of Mercuric Nitrate.—Mercuric nitrate has, as in the
reaction with acetylene, a favourable effect on the rate of absorption
of ethylene and hence on the speed of interaction, and considerably
increases the yield of nitroform.   The effect of the mercury salt is
complex, but is largely to prevent the alternative reaction of simple
oxidation, thus increasing proportionally the addition reaction
producing the nitro-alcohol.   Side reactions are considerably
reduced in its presence.   A higher concentration of mercuric nitrate

was required to produce the maximum absorption of ethylene and the maximum yield of tetranitromethane than in the case of acetylene, and 0·66% was found to promote the best results. The ratio of Carbon dioxide evolved/Ethylene absorbed approached unity under the optimum conditions, but exceeded it only in exceptional cases.

Isolation of β-*Nitroethyl Alcohol.*—The product of the reaction between ethylene and fuming nitric acid was diluted with water, neutralised with sodium carbonate, and extracted with ether. From the washed and dried extract, by fractional distillation under diminished pressure, β-nitroethyl alcohol was obtained as a faintly yellow oil, b. p. 117—121°/30—35 mm.

The amount of nitroform which can be extracted and estimated by the ordinary procedure is always in excess of the alcohol, the ratio of alcohol to nitroform being approximately 1 : 2·4. The presence of mercuric nitrate seems to have little effect on this ratio. If, however, the estimation of the two compounds be carried out before the completion of the reaction, this ratio is markedly different; the amount of nitroform which can be isolated at such stages is appreciably less than that at the end of the reaction, whereas the amount of nitro-alcohol is not. The ratio of the two substances when half the normal quantity of ethylene had been passed was unity. Two facts of importance emerge from these data. Nitroform is produced subsequently to and, it would appear, at the expense of the nitro-alcohol, and the formation of nitroform takes place largely towards the end of the passage of the hydrocarbon.

TABLE III.

Relation between β-nitroethyl alcohol and nitroform.

Experiment.	β-Nitroethyl alcohol (g.).	Nitroform (g.).	$\dfrac{\text{Nitro-alcohol}}{\text{Nitroform}}$.
95% HNO₃. No Hg ⎫ 95% HNO₃. Hg ⎬	1·98 4·59	4·6 11·4	1 : 2·32 1 : 2·48
95% HNO₃. No Hg ⎫ (½ ethylene passed) ⎬ 95% HNO₃. Hg ⎭	1·36 3·38	1·9 5·14	1 : 1·4 1 : 1·52