TABLE 2
RATIO OF 1,2,4- TO 1,3,5-TRIALKYLBENZENES FORMED IN THE CYCLOTRIMERIZATION OF PROPYNE, BUTYNE-1, AND PENTYNE-1 AT DIFFERENT TEMPERATURES

Starting alkyne	Ratio of 1,2,4 to 1,3,5 isomers formed	
	100–300°C	300–550°C
Propyne	3.7	1.6
Butyne-1	3.6	1.4
Pentyne-1	1.2	1.0

respond with higher disproportionation conversions supports this interpretation. Quantitatively the most important reaction is cyclotrimerization to benzene derivatives. At moderate temperatures the selectivity of this reaction for the α-alkynes investigated is very high. At high temperatures other reactions occur besides cyclotrimerization and disproportionation. Thus, in an experiment with propyne at 465°C, 20% of the liquid products were xylenes; this was confirmed by NMR-spectrometry.

Table 2 summarizes the ratio of the isomers formed by cyclotrimerization. The products of cyclotrimerization of the α-alkynes investigated were mainly 1,2,4- and 1,3,5-trialkylbenzenes; the formation of 1,2,3-isomers could be neglected. Only at temperatures above 300°C were small amounts of the 1,2,3-isomer formed; however, they never exceeded 2% by weight of the total amount of trimers.

According to Whitesides and Ehmann (*4*) mechanisms of cyclotrimerization can be divided into two groups:

(*a*) cyclotrimerization via a cyclobutadiene intermediate,

(*b*) cyclotrimerization via other mechanisms. The authors derived the conclusion that for α-alkynes the theoretical product distribution in *case* (*a*) amounts to (1,2,3) : (1,2,4) : (1,3,5) = 1:5:2 and in *case* (*b*) to 0:3:1. They infer that the cyclobutadiene mechanism can be rigorously excluded when 1,2,3-trialkylbenzene is not a reaction product. Following this reasoning it is clear from the results shown in Table 2 that mechanism (*a*) is excluded at temperatures below 300°C. At higher temperatures the cyclobutadiene mechanism is not rigorously excluded; in our opinion, however, it is more probable that the small amounts of the 1,2,3-isomer have been formed by side reactions and consecutive reactions, which evidently occur.

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A Test for the Development of Protonic Acidity in Alumina at Elevated Temperatures

Various acid catalyzed reactions such as alcohol dehydration, double bond and skeletal isomerizations, and hydrocarbon cracking are catalyzed by alumina. The acidic properties of aluminas have frequently been studied by ir-spectroscopic methods (*1–4*) using pyridine as a base (pK_a = 5.25 at 25°C in aqueous solution) and it has been shown that aluminas never form the pyridinium ion, indicating that the number of sufficiently strong protonic sites, if existent at all, must be too low to be detected. With the more basic ammonia ($pK_a = 9.25$ at 25°C in aqueous solution) the formation of an NH_4^+ species has been reported (*5*, *6*), so that some very weak protonic acid sites may exist on the alumina surface. In these experiments the spectra were always recorded at room temperature. It had therefore been speculated that alumina might be a strong protonic acid only at the higher temperatures of catalytic reactions (*7*). The change from a mechanism of E2-type to one of E1-type in the dehydration of alcohols with increasing temperature was interpreted analogously (*8*). An activation of surface hydroxyls with increasing temperature ($T > 360°C$) was indeed observed by Ward (*9*) for hydrogen-Y zeolites.

To test whether there is an increase in protonic acidity with increasing temperature we have now recorded at elevated temperatures the ir spectra of pyridine adsorbed on alumina surfaces in the presence of the vapor. The spectra were recorded with a Perkin-Elmer spectrophotometer Type 225 using a cell which was described previously (*10*). The aluminas used were a δ-Al_2O_3 (Degussa Type P 110 C 1) which was prepared by flame hydrolysis from $AlCl_3$, and a η-Al_2O_3 which was prepared by pyrolysis of bayerite. The temperature of the cell was measured at the ir windows; the temperature of the alumina could not be detected directly but it should be higher than (or equal to) the cell temperature. The adsorbents had been dehydroxylated *in vacuo* at 400 and 500°C prior to the adsorption of pyridine. Spectra were recorded at cell temperatures between 40 and 300°C.

The apparent transmission of the samples increased with increasing temperature due to the emission of the oxide at higher temperatures. Since only qualitative information was sought, this effect was not measured quantitatively in the present work. The spectra demonstrated the well-known formation of hydrogen-bonded and coordinately-bonded pyridine (*1–4*) in the presence of the vapor. With increasing temperature the intensity of the bands of hydrogen-bonded species decreased rapidly because of desorption, whereas the bands indicating coordination bonds were reduced in intensity only slowly (Fig. 1). Even at the highest temperatures no bands were observed around 1640 and 1540 cm^{-1}, which would have indicated the formation of the pyridinium ion. Even the addition of water vapor at 250°C only led to a displacement of pyridine. This result agrees with earlier observations (*1*, *2*, *4*), which demonstrated that the Lewis acid sites on alumina surfaces are not converted to Brönsted sites on addition of water. The same results were obtained with η-Al_2O_3 whose surface had been chlorinated by reaction with CCl_4 according to Basset *et al.* (*11*).

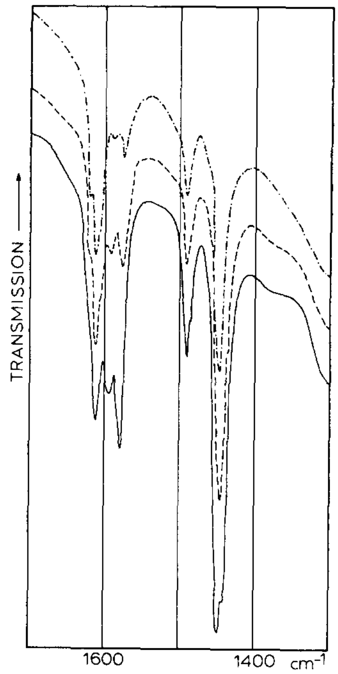

FIG. 1. Infrared spectra of pyridine adsorbed on δ-Al_2O_3 (pretreated at 500°C) in the presence of 27 mm Hg vapor recorded at different cell temperatures:
—— 43°C; ---- 150°C; -·-·- 250°C.

It must therefore be concluded that alumina surfaces do not develop a protonic acidity, at least at temperatures up to 300°C, that is strong enough to protonate pyridine. One might argue that the number of protonic sites was too low to be detected. The number of active sites for the cyclohexene isomerization, which could have been interpreted by means of a proton addition, has been measured recently by pyridine poisoning (*12*) and found to be sufficiently high (2 to 4 per 1000 Å^2) to be easily detectable by ir-spectroscopy. It thus seems that protonic sites on alumina cannot act as active sites in hydrocarbon reactions at temperatures below 300°C, since most reactants such as alkanes or alkenes have much lower basicities than pyridine.

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Chemisorption of Methanol and Electrical Conductivity Changes on Vanadium Pentoxide Catalysts

Vanadium pentoxide prepared by the decomposition of vanadyl oxalate (catalyst I) has a greater catalytic activity than that prepared by the decomposition of ammonium metavanadate (catalyst II) (*1–3*). Recently we have reported (*4, 5*) that catalyst I possesses more surface area, larger magnetic susceptibility and a greater concentration of V^{4+} ions than catalyst II and also a greater amount of oxygen becomes chemisorbed on catalyst I at a faster rate. The kinetics of chemisorption of methanol and the accompanying electrical conductivity changes on catalysts (I and II) have now been studied.

Catalyst I was prepared by the decomposition of vanadyl oxalate at 400°C for 4 hr in a continuous stream of air. Catalyst II was prepared by the decomposition of ammonium metavanadate at 400°C for 4 hr in a continuous stream of air. Chemisorption was studied in a conventional volumetric adsorption apparatus. The amount adsorbed was directly represented by the drop in pressure (Δp) in a constant volume system, without converting it to volume. The measurements were carried out by taking 10 g of powdered catalyst at an initial methanol pressure of 14 cm in the temperature range, 35–200°C. Absolute methanol, further purified and freed from moisture by distillation over magnesium metal, was used. To monitor electrical conductivity, the resistance of a pelleted sample was measured in the temperature range, 70–200°C, by an electronic dc voltmeter; details of the method