λ (A.) 2300 $\frac{2250}{2200}$

2150

2000

formaldehyde and hydrogen probably arise from side reactions.

$$CHO + CHO \rightarrow HCHO + CO$$

$$\searrow H_{\bullet} + 2CO,$$

the material balance requiring that $p_{C_sH_s} = p_{HCHO}$ $+ p_{\mathbf{H}_{1}}$

If the ethane does arise from the reaction between methyls, this excludes the reaction

$$CH_3 + CHO \rightarrow CH_4 + CO$$

as the chain termination. On the other hand, it does not exclude the alternative mechanism in which formyl radicals propagate the chain, when the reaction between methyl radicals would be the side Nevertheless, the weight of evidence is reaction. for methyl radicals as chain carriers. If that is the case, the above analysis suggests that the termination is, in fact,

$$\mathrm{CH}_3 + \mathrm{CH}_3 \rightarrow \mathrm{C}_2\mathrm{H}_6.$$

This view is further substantiated by the agreement between the constants determined, by the sector method, for the termination reaction in the photolyses of acetaldehyde¹ and of mercury dimethyl². The observed frequency factors, of the same order as the collision frequency, do not, however, agree with the steric factor 5×10^{-3} found by Marcus and Steacie³ for the same reaction.

We have recently learned that Danby, Buchanan and Henderson⁴ have carried out, independently, extensive mass spectrometric analyses on the products of the reaction in its initial stages and have reached the same conclusion about the chain-ending process.

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¹ Dodd, R. E., Trans. Faraday Soc., 47, 56 (1951). ² Gomer, R., J. Chem. Phys., 18, 998 (1950). ³ Marcus, R. A., and Steacie, E. W. R., Z. Naturforsch., 4a, 332 (1949). Danby, C. J., Buchanan, A. S., and Henderson, I. H. S., J. Chem. Soc. (in the press, rec. January 17, 1951).

Use of 95 per cent Ethyl Alcohol as a Solvent for Ultra-Violet Spectroscopy

In connexion with a problem on the determination of the ultra-violet absorption spectra of organic molecules dissolved in 95 per cent ethyl alcohol1, it was necessary to determine the suitability of the alcohol as a solvent in the region of 2000 Å. There is a report² that carefully purified 95 per cent ethyl alcohol³ is suitable for the region of 2000 A., although no experimental results were given. Observations in this region have been reported by MacLean, Jencks and Acree⁴ for ordinary commercial 95 per cent ethanol, and they find that unpurified alcohol ts completely opaque in this region.

It seemed to be of interest, then, to determine the transmission of purified 95 per cent ethanol down to 2000 A. The results are shown in Table 1. The percentage transmission of the alcohol was determined with the aid of a Beckman quartz spectrophoto-

	Table 1			
(a) % Transmission	(b) % Transmission	(c) % Transmission		
 62	68.2	83.8		
54	59.2	76.5		
46	50	67.5		
36	40	57-5		
28.2	33.8	45.5		
17	18.5	29.2		
10.8	10.9	18.9		

meter equipped with a Nestor hydrogen lamp. The transmission of the alcohol at the various wavelengths was measured against distilled water, and it was assumed that the transmission of the water in this region was 100 per cent. Column a gives the results for the transmission of the untreated commercial alcohol; column b is for the alcohol after refluxing with dilute sulphuric acid and distillation², column c after treatment of the acid-treated alcohol with silver oxide and distillation. Repetition of the purification procedure with this alcohol did not materially change the values reported in column c.

Pirlot⁵ has recently described another method for the purification of alcohols for ultra-violet spectroscopy, consisting in treatment with iodine, removal of the iodine with zinc and then passage of an alkaline solution of the alcohol over a column of activated charcoal. The results for ethyl alcohol in the region of 2000 A. were not reported; but from the data for the transmission of methyl alcohol in this region, it would seem that the values for ethyl alcohol treated in this fashion would be similar to those reported now.

Table 9

λ(Α.)	(a) % Transmission	(b) % Transmission
2300	75.5	79.8
2250	68.0	70.8
2200	60	62.3
2150	50.8	54.0
2100	30.0	43.0
2050	9.0	18.2
2020		9.1
2000		3.5

An investigation of the transmission of commercial absolute alcohol was also made. The results are shown in Table 2. Column a shows the transmission for the untreated alcohol; column b shows the transmission after refluxing with dilute sulphuric acid, distillation and treatment of the distillate with silver oxide. The first and last 15 per cent of each distillate was discarded.

On the assumption that the solvent should transmit at least 50 per cent of the radiation² to be suitable at any particular wave-length, it would appear that even carefully purified 95 per cent ethanol is not a suitable solvent for work below 2100 A., and absolute alcohol is not suitable below 2120 A.

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- ⁴ MacLean, Jencks and Acree, J. Res. Nat. Bureau of Standards, 84, 271 (1945).
- ^b Pirlot, Bull. Soc. Roy. Sci. Liège, 18, 115 (1949).

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