A NOTE ON COMBUSTION PROPERTIES OF CHROMIUM TRIOXIDE

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Chromium trioxide has been found to be powerful oxidising agent for supporting the combustion of many organic fuels like alcohols, aldehydes and ketones. Ignitability of butanols follows the order, *n*-butanol > *sec*-butanol > *tert*-butanol. Chromium trioxide supports combustion by supplying the necessary oxygen by its own dissociation. During the combustion, chromium trioxide changes from Cr^{+6} to Cr^{+3} oxidation state.

Transition metal oxides have been widely used as oxidising agents under wide variety of conditions for liquid-phase oxidation of various organic compounds[1]. Chromium trioxide amongst them, is one of the most attractive and powerful oxidising agents. It can also oxidise inorganic compounds. Although the chemistry of oxidation process in solution involving chromium trioxide is well known, the behaviour of the same in supporting the combustion has received little attention. It has been observed that when chromium trioxide comes in contact with several organic compounds like alcohols, aldehydes and ketones etc., it causes spontaneous ignition with the appearance of a flame. With this interesting characteristic, it can be a useful material in the field of propellants and explosives. The purpose of the present communication, therefore, is to examine the ignitability of some fuels with chromium trioxide and to throw some light on the mechanism of the ignition process.

EXPERIMENTAL

Pure laboratory grade CrO_3 (B.D.H.) in powder form was used. It was always stored in a desicator to prevent its contact with moisture. Laboratory grade organic compounds (Riedel/B.D.H) like acetone, acetaldehyde, ethylalcohol, methylethyl ketone, methyl isobutyl ketone, γ-butyrolactone, furfuraldehyde, cyclohexanone, croton aldehyde, 2-ethoxy ethanol, isopropyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, acetophenone, benzaldehyde, benzyl alcohol and furfuryl alcohol were used as such without any further purification.

Dry powdered chromium trioxide (approx. 800 mg) was spread in a porclain dish (dia 6·35 cm) and the fuel (0·5 ml) was dropped at the center of it with the aid of a wide mouth dropper. The appearance of the flame could be observed visually.

RESULTS AND DISCUSSION

It was observed that most of the compounds listed above except furfuryl alcohol and *tert*-butyl alcohol burn spontaneously with chromium trioxide. It was also observed that the residue in the dish, after combustion, becomes bright green in colour. It is well known that chromic oxide (Cr^{+3} oxidation state) has bright green colour and therefore change over from dark purplish colour before ignition to dark green colour after ignition indicates the transition of Cr^{+6} to Cr^{+3} oxidation state according to the following equation.

$$4\,CrO_3 = 2\,Cr_2O_3 + 3O_2$$

The oxidation via the formation of chromic acid ($HCrO_4$) is ruled out here in view of the fact that almost no water was present in the system. The oxygen liberated during the formation of chromic oxide may be utilised for the oxidation of organic compounds and therefore oxidation of the compounds must take place during combustion.

If the combustion occurs via the oxidation process then aliphatic alcohols should get oxidised more easily compared to the corresponding aldehydes, ketones and acids[3]. In order to check the above mechanism, the ignitability of alcohols, aldehydes, ketones and acids was tested by diluting them

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with water and finding out the optimum percentage of the fuel wherein the combustion with flame starts appearing. The results are given in Table 1. Table 1 very clearly shows that alcohol burns more easily compared to a ketone and that the corresponding acid does not burn at all. A careful look at the ignitability of butanols (Table 1) reveals that the ignitability follows the following order for the ease of burning with chromium trioxide.

$$n\text{-butanol} > sec\text{-butanol} > tert\text{-butanol}$$

It may be noted that the above order is also the order by which the butanols can be oxidised[3]. The ignition tests were extended to aromatic and heterocylic compounds. In both these cases the alcohols are less easily oxidised compared to the aldehydes[1,3] and the same order was also observed for their ignition behaviour (Table 1).

Table 1

Effect of dilution on ignition†

Compounds	Fuel required for ignition to occur (Vol %)	Remarks
Ethyl alcohol	55	S
Acetone	65	I
	70	S
Acetic acid	100	no burning
n-Butanol	40	S*
sec-Butanol	50	S**
tert-Butanol	100	I
Benzoyl alcohol	80	S
Benzaldehyde	55	S
Furfuryl alcohol	100	no burning
Furfuraldehyde	100	Spontaneous

†The solutions were well shaken just before the experiment in case of the poor miscibility of the liquids.

S=Spontaneous ignition : where the ignition delay (time between the mixing of the components and the appearance of flame) could not be measured with the help of a stop watch.

I=Ignition with measurable delay.

*At 20—40% Ignition takes place but the flame is not sustained.

**At 30—50% Ignition takes place but the flame is not sustained.

The above ignition experiments very clearly indicate that combustion occurs via the oxidation process and that the necessary oxygen, required for supporting the combustion, is supplied by the dissociation of chromium trioxide.

REFERENCES

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