

Table 1. INTERPLANAR SPACINGS OF CARBIDES

hkl	Boro-carbide*		Cr ₂₃ C ₆ †	
	d (A.)	Intensity	d (A.)	Intensity
311	3.187	W		
222	3.055	W		
400	2.644	W		
420	2.367	S	2.380	MS
422	2.161	S	2.172	M
333, 511	2.037	VS	2.048	S
440	1.872	S	1.882	M
531	1.792	S	1.800	M
600, 442	1.765	M		
620	1.674	VW	1.683	W
533	1.613	W		
622	1.595	MW	1.605	MW
640	1.466	VW		
800	1.325	W		
644, 820	1.284	W	1.291	M
660, 882	1.248	M	1.255	MS
555, 751	1.222	M	1.229	M
840	1.183	W		
753, 911	1.162	W	1.168	M
931	1.111	W		
844	1.082	M	1.086	S
933	1.065	MW	1.070	MW
1,040	0.9830	W	0.9883	M
1,042	0.9668	W	0.9716	M
775	0.9549	W	0.9597	W
880			0.9403	W
971	0.9254	M	0.9300	S

* Present data, from X-ray diffractometer, cobalt radiation.
 † Goldschmidt (ref. 3); interplanar spacings converted to angstroms.
 Key to intensities: VS = very strong; S = strong; MS = medium to strong; M = medium; MW = medium to weak; W = weak; VW = very weak.

This new boro-carbide has been found in several of the samples in the range 1½–2½ per cent boron and 2½–4½ per cent carbon. Analogy with the Westgren carbides would suggest a composition corresponding to Fe₂₃(C,B)₆. The question as to whether this boro-carbide can exist over a substantial range of compositions is not settled; however, all samples so far observed have the same lattice parameter within the stated error of ± 0.02 Å.

If we choose to consider the hypothetical carbide Fe₂₃C₆, then it may be said that Westgren and Goldschmidt have produced carbides in which chromium, molybdenum or tungsten has been substituted for iron. To the best of our knowledge the present boro-carbide is the first reported case in which another element (boron) has been substituted for carbon in this structure. This type of carbide has generally been found in, and regarded as characteristic of, some stainless and high-speed steels. It is possible that the appearance of boron therein may eventually shed some light upon the pronounced influence of boron upon the hardening properties of steel.

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¹ Westgren, A., *Jernkontorets Annaler*, **117**, 501 (1933).
² Goldschmidt, H. J., *J. Iron and Steel Inst.*, **160**, 345 (1948).
³ Goldschmidt, H. J., *Metallurgia*, **40**, 103 (1949).

Effect of Nitrogen Dioxide on the Thermal Decomposition of Ethyl Nitrite

The value of gas chromatography as a technique for the analysis of the minute quantities of products formed during the kinetic studies of gas reactions is well illustrated by recent work on the gas-phase reaction between ethyl nitrite and nitrogen dioxide. Studies of the behaviour of ethyl nitrite, ethyl nitrate

and water on a partition column of kieselguhr wetted with di-butyl-phthalate and eluted with nitrogen revealed that a complete separation of a mixture of the esters and water can be achieved. Using gas chromatography, it has thus been possible to identify three major components, namely, ethyl nitrite, ethyl nitrate, and water, in the residue from the reaction between ethyl nitrite and nitrogen dioxide at about 190° C. Few other micro-analytical techniques would have enabled this to be done so simply or so quickly.

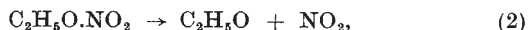
40 mm. of ethyl nitrite and 40 mm. of nitrogen dioxide were allowed to react in a glass vessel of approximately 90 ml. capacity. The temperature of the reaction was about 190° C. Analysis of the residues from interrupted runs for periods up to one hour are given in the table. These show that the quantity of ethyl nitrate produced reaches a maximum after 10 min. and becomes negligible after one hour. The residue of ethyl nitrite was identified on all chromatograms but not quantitatively estimated.

Time of reaction (min.)	2.0	2.8	3.5	5.5	7.5	11.0	15.0	25.0	45.0	60.0
Pressure of ethyl nitrate (mm. mercury)	1.8	2.5	3.9	4.4	5.1	5.3	4.6	3.4	0.9	≈ 0.0

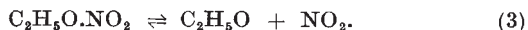
The formation of ethyl nitrate during the decomposition of ethyl nitrite in the presence of nitrogen dioxide affords direct evidence in favour of the reaction:



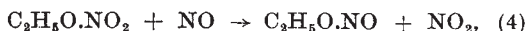
originally suggested by Phillips¹ in explanation of the inhibition of the thermal decomposition of ethyl nitrate by nitrogen dioxide. In this event, it is possible that previous values obtained for the rate of decomposition of ethyl nitrate do not refer to the rate of the reaction:



since the decomposition involves the equilibrium



These conclusions would mean that the effect of nitric oxide on the decomposition of ethyl nitrate previously ascribed² to the reaction:



is probably due to the occurrence of



proceeding in preference to (1) in the presence of initially added nitric oxide. This would also explain Levy's³ observation of the production of ethyl nitrite (in quantities greater than 70 mol. per cent) during the normal decomposition of ethyl nitrate.

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¹ Phillips, L., *Nature*, **165**, 564 (1950).
² Pollard, F. H., Marshall, H. S. B., and Pedler, A. E., *Nature*, **171**, 1154 (1953).
³ Levy, J., *J. Amer. Chem. Soc.*, **76**, 3254 (1954).