Catalysis by Coordinatively Unsaturated Surface Compounds of Chromium(II), Iron(II), Cobalt(II) and Nickel(II) on Silica Gel. I. Decomposition of NO and NO Reduction by CO

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The coordinatively unsaturated surface compounds of chromium(II), iron(II), cobalt(II) and nickel(II) on silica gel catalyse the reduction of NO by CO and, with the exception of chromium(II), the decomposition of NO. The catalytic activity increases from nickel(II) to chromium(II) (reduction) and from nickel(II) to iron(II) (decomposition). During the reduction of NO by CO, N_2O is produced at lower and N_2 at higher temperatures. On the basis that NO is chemisorbed by these surface compounds a reaction model is set up, in which the coordinatively unsaturated surface compounds act as the catalytic center. This model is supported by the poisoning effect of water and by the fact that iron(II) samples with low pretreatment temperatures (300 and 500 °C) have no catalytic activity.

The four coordinatively unsaturated surface compounds of chromium(II),[1] iron(II),[2] cobalt(II)[3] and nickel(II)[4] on silica gel can each adsorb two molecules NO per metal ion at room temperature.[5] This observation indicates that these surface compounds might be catalytically active, as the first step in any catalytic reaction involving nitric oxide must be the chemisorption of NO.[6]

The strong interest in catalytic removal of nitrogen oxides from automotive exhaust gases[7] has made us concentrate our investigation on two reactions. The first is the decomposition of NO to N_2 and O_2, the second is the reduction of NO by CO to N_2 (and CO_2). From these investigations we also hope to obtain some understanding of the role of the electronic structure of the metal ion for the catalytic activity in the series of coordinatively unsaturated surface compounds.

EXPERIMENTAL

The chromium(II) surface compound was prepared by impregnating purified[8] silica gel "Merck 7733" (specific surface area approximately 600 m^2/g) with a solution of chromium(VI) oxide in water, drying this mixture at 120 °C in air and afterwards heating it in vacuum to 800 °C in a quartz tube. At that temperature oxygen was applied to the sample, which was then cooled down to 400 °C. After evacuation the chromium(VI) surface compound was reduced by CO. The samples of the coordinatively unsaturated surface compound of chromium(II) on silica gel so produced had obviously the same activity as those described in Ref. 8; for instance chemiluminescence during reaction with O_2 or the colour change from green to blue on adsorption of N_2 was the same as described there. The chromium concentration in the sample was 0.6 %.

The preparations of the coordinatively unsaturated iron(II) and cobalt(II) surface compounds on silica gel have been described previously[2,3] and the corresponding nickel(II) compound was prepared in the same way as that of cobalt(II).[3] The iron content of the samples was 0.7 %, while the cobalt(II) and nickel(II) contents were 0.6 %.

To perform the catalytic reactions the samples were placed in a column with an inner diameter of 8 mm and a heated length of 200 mm. The gases NO or NO/CO were dried by molecular sieve and phosphorus pentoxide before passing over the sample with a speed of 10 ml/h. In the NO decomposition experiments NO_2 was removed from the produced gas mixture by moist potassium hydroxide[9] and the remaining NO and the catalytically produced N_2 and N_2O determined with a Perkin-Elmer F 17 gas chromatograph. The separation column was filled with molecular sieve 13 X, mesh 45/60. The error of these measurements was within

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3 %. In the case of the NO reduction by CO the gases N_2, N_2O, NO and CO were determined.

RESULTS

NO decomposition. During an examination of the decomposition of NO five reactions have to be taken into consideration:

1. $2NO \rightarrow N_2 + O_2$

2. $2NO \rightarrow N_2O + 1/2 O_2$

3. $N_2O \rightarrow N_2 + 1/2 O_2$

4. $2NO + O_2 \rightleftharpoons 2NO_2$

5. $2NO_2 \rightleftharpoons 2N_2O_4$

The equilibrium of reactions 4 and 5 are shifted to the right only at relatively low temperatures, so that the gas mixture in the column contains only NO, N_2 and perhaps N_2O at the temperatures where catalytic activity was observed.

The catalytic decomposition of NO takes place on the coordinatively unsaturated surface compounds of iron(II), cobalt(II) and nickel(II) at temperatures higher than 300 °C and is most effective with the iron(II) surface compound, as is shown in Fig. 1. With this surface compound a maximum conversion of 75 % was reached at 750 °C (Fig. 2).

In contrast to these three surface compounds no catalytic activity was observed with the chromium(II) surface compound. However, the
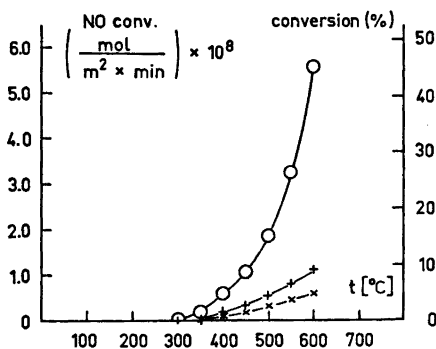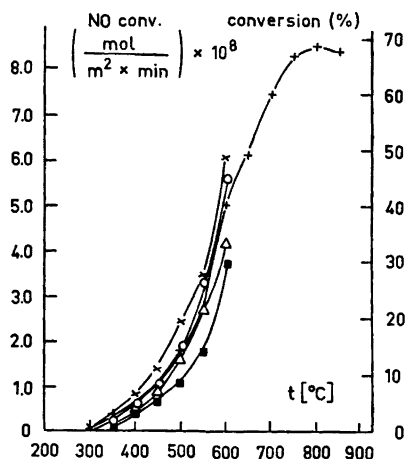

Fig. 2. Decomposition of NO over samples with different iron(II) concentrations on silica gel as a function of temperature. ×, 1.4 % Fe; +, 1.05 % Fe; O, 0.7 % Fe; △, 0.35 % Fe; ■, 0.175 % Fe.

production of N_2O and a small quantity of N_2 was observed between 150 and 250 °C. The N_2O may be produced according to reaction 2 in the above reaction list. In this case the accompanying O_2 is a strong poison for the chromium(II) surface compound, because the O_2 oxidises the chromium(II) to chromium(VI).[1,8] Only small amounts of N_2O and N_2 are produced by the surface compounds of iron(II), cobalt(II) and nickel(II) between 150 and 300 °C.

Fig. 1. Decomposition of NO over iron(II), cobalt(II) and nickel(II) on silica gel as a function of temperature. O, 0.7 % Fe; +, 0.6 % Co; ×, 0.6 % Ni.
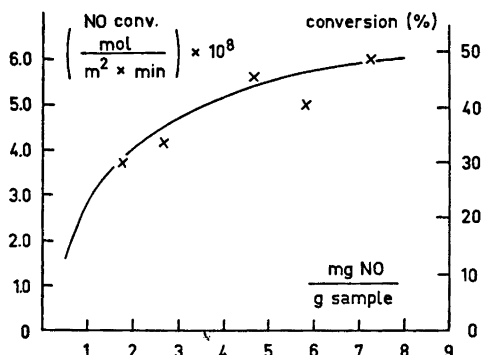

Fig. 3. Decomposition of NO at 500 °C over samples with different iron(II) concentrations on silica gel *versus* NO adsorption at 0 °C and vacuum (1 Torr).
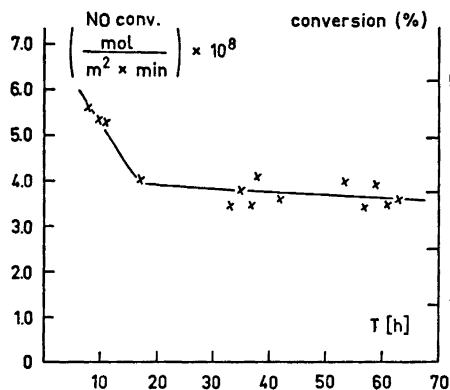
Fig. 4. Decomposition of NO at 600 °C over 0.7 % iron(II) on silica gel *versus* time.

The effect of different iron(II) concentrations on the conversion rate of the catalytic decomposition of NO is relatively small (Fig. 2). Obviously there exists no linear relation between the rate of the catalytic conversion of NO and the NO adsorption of samples with different iron(II) content (Fig. 3). A possible explanation of the latter two effects may lie in a slow diffusion of the gas molecules to and away from the catalytic sites since the mean pore diameter of the silica gel used here is relatively small (60 Å). Another explanation may be that only some of the surface iron(II) ions, which adsorb NO, are catalytically active.
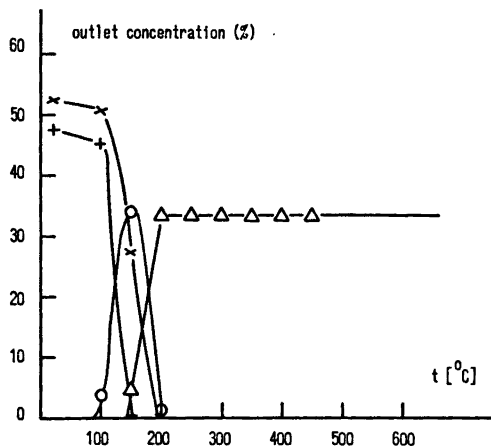
When run a long time, as shown in Fig. 4, the rate of decomposition of NO decreases over a period of approximately ten hours and remains constant afterwards at nearly half the value of the original conversion rate. If samples of iron(II) on silica gel, which were pretreated in vacuum at only 500 °C and not at 1000 °C as used before, were applied, no catalytic conversion of NO was detected up to 600 °C. It was also found that water is a strong poison for the above reaction. If it is assumed that only the coordinatively unsaturated iron(II) ions are the catalytically active centers the last two observations support the reaction scheme [2] put forward for the preparation of this species. There are no observations limiting this conclusion to iron(II) only and so it may be extended to cobalt(II) and nickel(II).

NO reduction by CO. Three reactions can be involved in the catalytic reduction of NO by CO:

1. $2NO + 2CO \rightarrow N_2 + 2CO_2$

2. $2NO + CO \rightarrow N_2O + CO_2$

3. $N_2O + CO \rightarrow N_2 + CO_2$

As shown in the Figs. 5 − 8 N_2O is produced in the beginning of the reduction at relatively low temperatures and is replaced as a reaction product at higher temperatures by N_2. The catalytic activity decreases from chromium(II) to nickel(II), as indicated by the increase in the
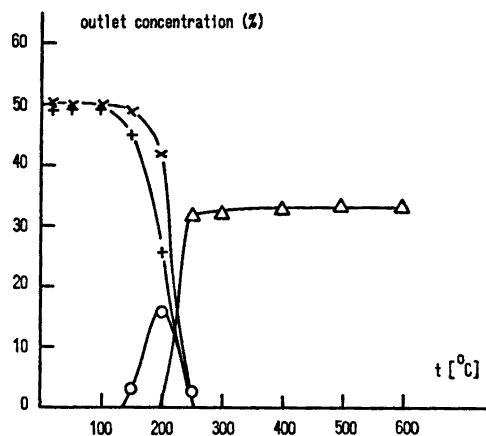

Fig. 5. NO reduction by CO over chromium(II) on silica gel *versus* temperature. ×, CO; +, NO; ○, N_2O; △, N_2.

Fig. 6. NO reduction by CO over iron(II) on silica gel *versus* temperature. ×, CO; +, NO; ○, N_2O; △, N_2.
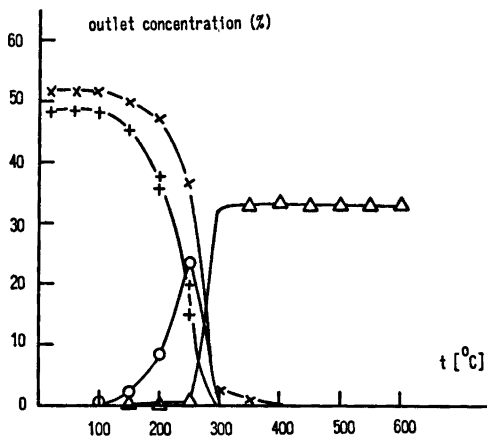
Fig. 7. NO reduction by CO over cobalt(II) on silica gel *versus* temperature. ×, CO; +, NO; ○, N_2O; △, N_2.
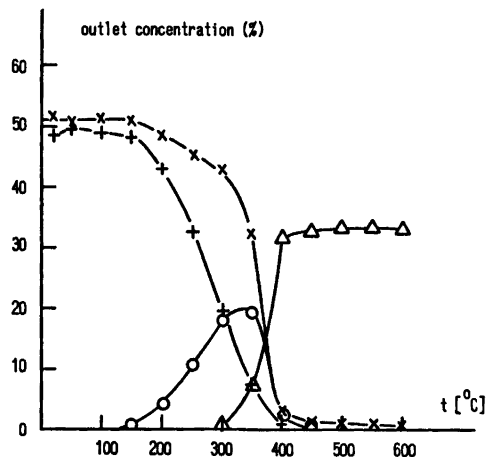

Fig. 8. NO reduction by CO over nickel(II) on silica gel *versus* temperature. ×, CO; +, NO; ○, N_2O; △, N_2.

temperature of the N_2O maximum and by the increase in the temperature of complete conversion of N_2. The decrease in the catalytic activity observed on going from iron(II) to nickel(II) is approximately the same as that during the catalytic decomposition of NO. It was observed that, after heating the samples to 600 °C under the catalytic process conditions, the temperature of the N_2O maximum and that of complete conversion to N_2 is about 50

°C higher than before in the case of iron(II), cobalt(II) and nickel(II). This temperature shift was not observed with chromium(II).

It was found that water is a strong poison for the catalytic reduction of NO by CO. As Figs. 9 and 10 show, the catalytic activity in this reaction decreases, when iron(II) on silica gel is heated to only 500 °C in vacuum and vanishes if a pretreatment temperature of 300 °C is used. In the latter case it is interesting
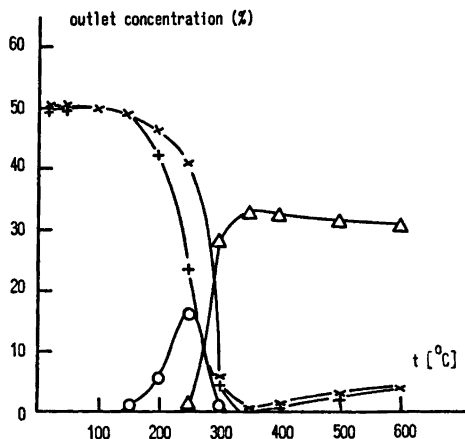

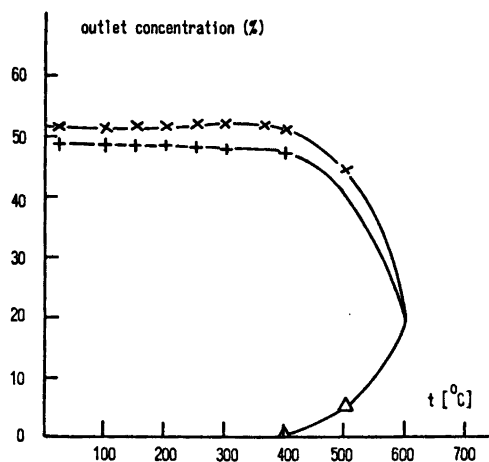*Fig. 9.* NO reduction by CO over iron(II) on silica gel (pretreatment temperature 500 °C) *versus* temperature. ×, CO; +, NO; ○, N_2O; △, N_2.

Fig. 10. NO reduction by CO over iron(II) on silica gel (pretreatment temperature 300 °C) *versus* temperature. ×, CO; +, NO; △, N_2.

Table 1. Results of IR measurements on NO adsorbed by coordinatively unsaturated transition metal ions on silica gel.

Transition metal ion	$\bar{v}_{a(NO)}$ (cm^{-1})	$\bar{v}_{s(NO)}$ (cm^{-1})	$\dfrac{\bar{v}_{a(NO)} + \bar{v}_{s(NO)}}{2}$ (cm^{-1})	Angle between NO's (°)
Chromium(II) [5b]	1747	1865	1806	126 [a]
Iron(II) [2]	1802	1870	1836	130
Cobalt(II) [3]	1797	1875	1836	110
Nickel(II) [4]	1832	1878	1855	99

[a] This angle was calculated from the intensity ratio reported by Zecchina *et al.*[12]

that, when some water is stripped off the iron(II) surface compound at temperatures higher than 300 °C, not N_2O but N_2 is the product of the catalytic reduction of NO. A comparison of the results given in Figs. 6, 9 and 10 indicates that during the last treatment more or less the same catalytic center is produced as with the vacuum heat treatment at 1000 °C described in Ref. 2. This leads again to the conclusion that only the coordinatively unsaturated iron(II) surface compound can be the catalytic center. It is assumed that this conclusion can again be extended to the other three surface compounds used in the above experiments.

DISCUSSION

It was noted above that the four coordinatively unsaturated surface compounds of chromium(II), iron(II), cobalt(II) and nickel(II) on silica gel each adsorb two molecules NO per surface metal ion.[5] As Table 1 shows all four surface compounds have two IR bands, the separation of which decreases from chromium(II) to nickel(II). The arithmetic mean value of the two IR absorptions increases in that direction. The angle between the two adsorbed NO molecules, as calculated from the intensities of the IR bands,[10] decreases in the same direction. Indeed at high temperatures there exists some evidence that either two molecules or none are bound to the metal surface ion.[2,11a] Furthermore, attention should be directed towards the observations of Zecchina *et al.*[12] that some additional molecules (but not NO) can be adsorbed to the bis-NO surfac complex, at least at low temperatures. This
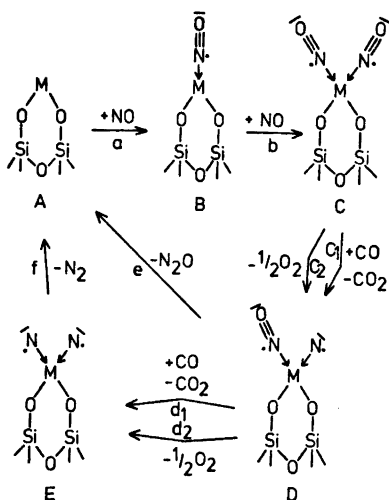
is an indication of a possible five-coordination complex at the reduction (*cf.* below).

In order to discuss the bond between the adsorbed NO and the metal surface ion, a coordinative bonding is very likely, as NO wavenumbers between 1700 and 1870 cm^{-1} are assigned to such a chemisorption.[13] Because the unpaired electron occupies an antibonding π^* orbital, increasing the electron density of the $N - O$ bond will decrease the bond strength and the frequency of the NO stretching vibration. If the electron density is decreased the bond strength and the wavenumber of the NO vibration will increase. In our case of NO adsorbed at the coordinatively unsaturated surface compounds the arithmetic mean value decreases from nickel(II) to chromium(II) indicating an increase in electron density at the $N - O$ bond and an increasing electron donation from the metal ion.

This effect is in contrast to the number of d-electrons, which decreases from nickel(II) (d^8) to chromium(II) (d^4). However, a parallel effect between the ease of losing electrons (exemplified by the charge transfer spectra of the aqueous complexes, *cf.* Dainton[14]) and the back bonding can be stated.

A reaction mechanism of the catalytic decomposition of NO and the catalytic reduction of NO by CO should contain the reaction steps shown in the scheme. Some of these steps were pointed out before by other authors.[11]

The reactions c_1 and d_1 may use the above-mentioned additional free coordination site at the transition metal ion, the fifth, as the four others are used by two oxygen ligands from the surface of the silica gel and by two nitrogen ligands, respectively. The structures

A   +NO a →   B   +NO b →   C

f ↑ $-N_2$ e ↙ $-N_2O$ $-\tfrac{1}{2}O_2$ (C2) $\genfrac{}{}{0pt}{}{+CO}{-CO_2}$

E $\genfrac{}{}{0pt}{}{+CO}{-CO_2}$ d1   d2 $-\tfrac{1}{2}O_2$ D

D and E may be stabilised through two effects. One is a "back-bonding" from a metal d-orbital to an empty orbital of the N atom. We presuppose an sp^3 hybridization in the discussion, but perhaps other orbital combinations may be better. This effect will follow the trend discussed above, i.e. Cr, Fe, Co and Ni. The second effect is the formation of a three-center N—M—N bond housing the odd electrons of the nitrogen atoms.

This model allows us to understand how the two nitrogen atoms can leave the complex as an N—N unit. The larger the part of the three-center bond that is dominated by the s-orbital contribution, the larger is the N—N bonding and the closer the two atoms will approach each other.

Stabilising the intermediate reaction states D and E would decrease the activation energies of the reactions c and d and result in an enhancement of the catalytic reactions in the direction from nickel(II) to chromium(II). The same effect may be expected from the decreasing N—O bond strength, because that will make it more easy, on one side for the CO to attack the chemisorbed NO and on the other side for the N—O bond to be split.

From the scheme it can also be concluded that the production of N_2O or N_2 will depend on the relation of the two rates of reactions e and $d_{(1,2)}$. If reaction e is faster than reaction d N_2O will be produced, in the reverse case

N_2, and if both reaction rates are equal N_2O and N_2 will be produced in the same amount.

Comparing the discussion of the scheme with the observed reactions makes some additional remarks necessary. The decomposition of NO over chromium(II) on silica gel can be explained by the assumption that structure D in this case is very much stabilised and so much N_2O and so little N_2 are observed. As mentioned before the chromium(II) surface compound is destroyed during this reaction by the produced O_2. The fact that only a little N_2O is produced by the surface compounds of iron(II), cobalt(II) and nickel(II) at low temperatures in the decomposition of NO may be similarly explained by assuming that structure E in this case is more stabilised than structure D. This means that at the same time as the molecular bonds between N and O and the coordinative bonds between the metal and the adsorbed NO are weakened and at last split, new bonds between the oxygen atoms and the two nitrogen atoms are built. In such a case there would be no place for the building of N_2O.

Comparing the results from the catalytic reduction of NO by CO with the scheme, shows more straight-forward agreement, than in the above case. So the question may be asked if the proposed mechanism can also be applied to the catalytic reduction of NO by CO over transition metal oxides.[6] On one hand the N_2O at lower and the N_2 production at higher temperatures agree well with our observations. On the other hand there are no experimental results to support a model, like the coordinatively unsaturated surface compound as proposed here, describing a catalytic center of the decomposition of NO and of the catalytic reduction of NO by CO.

In the above scheme N_2O is not an intermediate reaction product, in contrast to ideas put forward in Ref. 6. Such an assumption seems not to be necessary. However, to be sure further experiments, especially with N_2O, should be performed.

REFERENCES

1. Krauss, H. L. and Stach, H. *Z. Anorg. Allg. Chem. 366* (1969) 34.
2. Rebenstorf, B. *Acta Chem. Scand. A 31* (1977) 547.
3. Rebenstorf, B. *Acta Chem. Scand. A 31* (1977) 208.
4. Rebenstorf, B. *Unpublished results.*
5. a. Krauss, H. L. and Weisser, B. *Z. Anorg. Allg. Chem. 412* (1975) 82; b. Zecchina, A., Garrone, E., Morterra, C. and Coluccia, S. *J. Phys. Chem. 79* (1975) 978; c. For NO adsorbed on iron(II), cobalt(II) and nickel(II) see Refs. 2, 3 and 4.
6. Shelef, M. and Kummer, J. T. *AIChE Symp. Ser. No. 115, 67* (1971) 74.
7. a. Weigert, W. M. and Koberstein, E. *Angew. Chem. 88* (1976) 657; b. McEvoy, J. E., Ed., *Catalysts for the Control of Automotive Pollutants, Adv. Chem. Ser.,* American Chemical Society, Washington, D. C. 1975, USA.
8. Krauss, H. L., Rebenstorf, B. and Westphal, U. *Z. Anorg. Allg. Chem. 414* (1975) 97.
9. Winter, E. R. S. *J. Catal. 22* (1971) 158.
10. Beck, W., Melnikoff, A. and Stahl, R. *Chem. Ber. 99* (1966) 3721.
11. a. Shih, S. S., Shihabi, D. S. and Squires, R. G. *Preprints of the Sixth International Congress on Catalysis, B 36*; b. Eisenberg, R. and Meyer, C. D. *Acc. Chem. Res. 8* (1975) 26.
12. Zecchina, A., Garrone, E., Ghiotti, G. and Coluccia, S. *J. Phys. Chem. 79* (1975) 984.
13. a. Terenin, A. N. and Roev, L. N. *Actes Congr. Int. Catal. 2nd, 1960, 2,* (1961) 2188; b. Terenin, A. and Roev, L. *Spectrochim. Acta 15* (1959) 946; c. Little, C. H. *Infrared Spectra of Adsorbed Species,* Academic, London, New York 1966.
14. Dainton, F. S. *J. Chem. Soc.* (1952) 1953.