Equation (5) involves v_r but the Reticulometer technique[3,4] normally combines swelling with modulus measurements and so a value of this parameter is available.

For comparison with equation (4), equation (5) may be rewritten

$$G_c \approx \frac{f}{\Delta h} \cdot \frac{h_0}{3A_0} \cdot \frac{1 + v_r^{\frac{1}{3}} \Delta h\, h_0^{-1}}{1} \tag{6}$$

Measurements made with NR gum vulcanizates[5] using approximations (4) and (6) in comparison with 'exact' results using the gaussian equation (1) show that (6) fits the data well over the required strain range, the approximate values of G_c being within two per cent of the exact values (*Table 1*).

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Complex Formation between Silver Perchlorate and Azo-bis-isobutyronitrile

In an earlier communication[1] we reported that the rate of thermal decomposition of azo-bis-isobutyronitrile (AZO) at 70°C is considerably enhanced by silver perchlorate and that the rate of initiation of the free-radical polymerization of methyl methacrylate by AZO shows a corresponding increase in the presence of the salt. At constant AZO concentration, it is found that the rate of polymerization increases initially with increasing [$AgClO_4$], but eventually reaches a plateau value independent of [$AgClO_4$]. Under these conditions the rate of initiation is approximately four times as great as that holding in the absence of silver perchlorate. Further, we showed that kinetic observations on the polymerization are consistent with the formation of a 1:1 $AgClO_4$–AZO complex which decomposes more rapidly at a given temperature than does pure AZO. Although a 2:1 complex could not be definitely excluded, this appeared less likely.

In this communication we report (*a*) the isolation of a 1:1 $AgClO_4$–AZO complex, and (*b*) an extension of the kinetic work outlined in the earlier paper[1].

(*a*) It was noticed that methyl methacrylate solutions containing both $AgClO_4$ and AZO become turbid on standing in the dark, and deposit a white precipitate on cooling to 0°C. Immediate precipitation occurs on mixing concentrated solutions of the two components in methyl methacrylate at room temperatures. Filtration, followed by washing with methyl methacrylate and ether gives the complex in a reasonably pure state. The compound may also be prepared in a similar way from solutions in ether or benzene. Elemental analysis gave the following figures: C 25·8, H 3·18, N 14·9, Ag 29·0 per cent, the calculated values for $AgClO_4$–AZO being C 25·8, H 3·20, N 15·1, Ag 29·1 per cent.

The complex is a white crystalline solid, m.pt 114°–115°C; it is insoluble in carbon tetrachloride, slightly soluble in methyl methacrylate and ether, and soluble in chloroform and acetone at room temperatures. Exposure to daylight causes slow decomposition and deposition of metallic silver. X-Ray powder photographs of the complex, AZO, and $AgClO_4$ are reproduced in *Figure 1*. Infra-red absorption spectra (KBr disc) reveal a shift in the nitrile band from 2 240 cm^{-1} in AZO to 2 263 cm^{-1}. The nitrile groups therefore appear to be involved in complex formation. It is not clear from the infra-red observations whether the azo group also participates. Nitriles are known to form complexes with derivatives of Ag^{I} very readily, but azo-compounds show much less activity in this respect[2]. However, Nuttall, Roberts and Sharp[3] have prepared an adduct $3PhN{=}NPh.2AgClO_4$. Hiramo, Miki and Tsuruta[4] have postulated complex-formation between AZO and aluminium triethyl, and they reported an upward shift in ν_{CN} of 31 cm^{-1}.

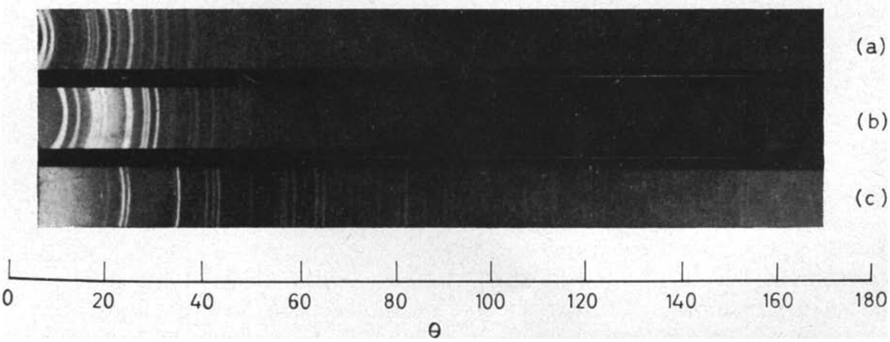

Figure 1—X-ray powder diagrams, CuK_α radiation, nominal radius of camera 4·5 cm. (a) AZO–$AgClO_4$ complex, (b) AZO, (c) $AgClO_4$

(*b*) Polymerization of methyl methacrylate initiated by AZO–$AgClO_4$ has been studied at four temperatures in the range 40° to 70°C. At each temperature the complete rate/[$AgClO_4$] relation for constant [AZO] was determined. Although the results were not sufficiently accurate to permit a reliable estimate of the variation of the equilibrium constant *K* with temperature to be made, it is clear that K decreases with increasing temperature, as expected. Since, at any temperature, initiation occurs exclusively by the complex when the rate has attained its plateau value, these experiments allow estimation of the difference in the activation energies (E) and the ratio of the frequency factors (A) for initiation by AZO and complex. It turns out that:

$$\left.\begin{array}{l} E_{\mathrm{AZO}} - E_{\mathrm{complex}} = 2{\cdot}7 \text{ kcal mole}^{-1} \\ A_{\mathrm{AZO}} / A_{\mathrm{complex}} = 12{\cdot}5 \end{array}\right\} \qquad (1)$$

Models show that it is easily possible to obtain a conformation of the AZO molecule (with a *trans* azo group) in which both nitrile groups can be bonded to a single silver ion. The azo group would appear to be too far from the silver to permit effective bonding. Formation of a cyclic complex in this way would introduce strain into the C—N=N—C linkages; relief of this strain in the transition state would tend to reduce the activation energy for decomposition. Further, it seems possible that in the transition state restrictions are imposed by the CN··Ag···NC bonds, so that degrees of freedom which develop in the transition state for the AZO decomposition are inoperative with the complex. The lower frequency factor for initiation by the complex is therefore understandable. The data in *Table 1* of ref. 1 suggest that the efficiency of initiation of the polymerization of methyl methacrylate at 70°C may be slightly higher for the complex than for AZO. This could arise from a reduction in the probability of recombination of two primary radicals brought about by their unfavourable disposition when coordinated to a silver ion.

We are extending these investigations to other related systems. Professor J. M. Robertson, F.R.S., of the Chemistry Department, University of Glasgow, has kindly undertaken a determination of the crystal structure of the AZO–$AgClO_4$ complex.

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Crystal Density, Crystallinity and Heat of Fusion of Poly (tetramethylene oxide)

THE determination of crystallinity in polymers from specific volume data is subject to a large error unless the crystal and amorphous phase values are known to high accuracy. The purpose of this communication is to give an early presentation of these constants for poly (tetramethylene oxide)