Table 2. EXTRACTION OF DIELDRIN AND ENDRIN (μgm./fly) : (*a*) FOR LIVING AND DEAD FLIES, RESPECTIVELY, AFTER 30 HR. ; (*b*) LIVING AND DEAD FLIES TOGETHER, AFTER 0, 40 AND 70 HR.

	Living	Dead
(*a*) Dieldrin	0·21	0·24
Endrin	0·26	0·28

	0 hr.	40 hr.	70 hr.
(*b*) Dieldrin	0·26	0·24	0·19
Endrin	0·23	0·17	0·14

by bioassay, by wire-loop applications to susceptible male flies (Table 2).

These limited data suggest that the different degrees of resistance developed to these two compounds do not depend on relative ease of elimination.

Common factor of the γ*-BHC–chlordane group*. The second question mentioned earlier was the problem of the common factor of the γ-BHC–chlordane group of insecticides. The compounds chlordane, aldrin, dieldrin, endrin and isodrin have obvious similarity in part of their molecules ; but γ-BHC appears quite different when represented graphically. When molecular models are prepared, however, it may be observed that five of the chlorine atoms of the chlordane group are arranged approximately symmetrically, with a sixth protruding from the centre. Models of the various isomers of hexachlorocyclohexane reveal a rather similar pentagon of chlorine atoms in the γ-form only (Fig. 2). It seems likely that this is the toxophore responsible for the high insecticidal activity of γ-BHC and the chlordane type insecticides. It may also explain the correlated resistance developed by flies to members of the group.

Additional evidence for this hypothesis was obtained by tests with a sample of octochloropropane, a highly chlorinated hydrocarbon not possessing a pentagonal arrangement of chlorine atoms. The median lethal concentration of this compound was found to be approximately 20 per cent for both the Omdurman and the laboratory strains. Thus, this substance is not highly insecticidal, nor does resistance to the γ-BHC–chlordane series alter the level of susceptibility to it.

Apart from chemical considerations, observations of the progress of intoxication in flies reveal similar features in γ-BHC and the chlordane group, which are quite different from signs of DDT poisoning. DDT causes continual, unco-ordinated movements ; but until a late stage of intoxication, the wings can function normally. Flies poisoned by γ-BHC or by a member of the chlordane group frequently show 'fanning' movements of the wings, insufficient to cause flight. At a late stage of intoxication, the legs are all tightly contracted under the body and the wings are usually deflected downwards (cf. Weismann[4]).

It is interesting to learn that, in mammals, there is an analogous difference in signs of poisoning by DDT as compared with those due to the γ-BHC–chlordane group of insecticides. Dr. J. M. Barnes, of the Medical Research Council Toxicology Research Unit, kindly allows me to quote his observations, as follows : "When these insecticides are dissolved in 'Tween 80' (polyoxyethylene sorbitan oleate) and injected intravenously into rats, there are two types of effect. DDT and methoxychlor, like phenol, produce widespread muscular twitchings. The intensity of the tremors depends on the dose. In the case of DDT, convulsions are relatively minor in severity and come as a cumulation of the violent tremors. Death may not take place for 1–2 hours. With *gamma* BHC, aldrin, endrin, dieldrin and chlordane, fine muscular twitchings are not seen. The outstanding feature is convulsions, of sudden onset and extreme violence, often starting within a few minutes of giving a dose that is just lethal. Death may occur during convulsions, or after a period of unconsciousness following the convulsions. Death, if it occurs, usually takes place within 10–15 minutes".

[1] Busvine, J. R., *Nature*, **168**, 193 (1951).

[2] Sacca, G., *Riv. Parassit.*, **14**, 97 (1953).

[3] Settatree, A. A., Thomas, S. L., and Yardley, V. A., *Nature*, **166**, 59 (1950).

[4] Weismann, R., *Z. Pflanzkrh. Pflanzsch.*, **58**, 161 (1951).

PHOTOLYSIS OF CHLORINE DIOXIDE AND ABSOLUTE RATES OF CHLORINE MONOXIDE REACTIONS

By F. J. LIPSCOMB, PROF. R. G. W. NORRISH, F.R.S., and DR. G. PORTER

Department of Physical Chemistry, University of Cambridge

THE absorption spectrum of chlorine monoxide was first detected in the photochemical reaction between chlorine and oxygen[1,2] and all direct studies of its reactions have so far been carried out on this system. The mechanisms of these reactions have been thoroughly elucidated, but[3] it has been necessary to express the absolute rates and concentrations in terms of an unknown constant which is numerically equal to the extinction coefficient of chlorine monoxide at a given wave-length. The evaluation of this constant would lead to absolute extinction coefficients of chlorine monoxide at all wave-lengths, absolute concentrations under any required conditions and absolute rate constants of the reactions of chlorine monoxide.

The extinction coefficient appears in these quantities because the observed parameter is an optical density, D_λ, of the reaction mixture at a given wave-length λ. We then have

$$D_\lambda = \varepsilon_\lambda c l,$$

where ε_λ is the extinction coefficient of chlorine monoxide at this wave-length, c is its concentration and l is the length of the absorption path. It is therefore possible only to measure the product $\varepsilon_\lambda c$ and not the separate quantities. Since the relative extinctions at two wave-lengths are easily obtained, all can be referred to a standard extinction, ε_s, at a wave-length of 2577 A., which is in the continuous region of the spectrum and is therefore insensitive to the exact wave-length and independent of the resolving power of the spectrograph.

The ClO radical is removed by the bimolecular process :

$$2\text{ClO} = \text{Cl}_2 + \text{O}_2 \; ; \qquad (1)$$

and the rate constant of this reaction is given by

$$k_1 = 7\cdot2 \times 10^4 \times \varepsilon_s \exp \frac{(0 \pm 650)}{RT} \text{ litre mole}^{-1} \text{ sec.}^{-1}.$$

To evaluate ε_8, the concentration of chlorine monoxide must be known and, in principle, this can be found by difference if the concentrations of the other species present are known. Thus, in the reaction between chlorine and oxygen, the only species which contain chlorine and which are present in significant concentrations are chlorine monoxide and chlorine, and the decrease in concentration of chlorine should lead directly to the concentration of chlorine monoxide. Unfortunately, owing to the low extinction of chlorine, this decrease of concentration was below the limit of detectability and it was therefore only possible to give a lower limit for ε_8 which was 310. Reasons were given for supposing that ε_8 was less than 3,000, but no further limits could be fixed by these experiments.

The extinction coefficient of chlorine dioxide is much greater than that of chlorine and is of the same order of magnitude as the above predicted values for chlorine monoxide. It follows that, if chlorine monoxide were detected during the photolysis of chlorine dioxide, the decrease in concentration of chlorine dioxide should be readily measurable. We have therefore investigated this reaction by the same experimental methods as were used to study the chlorine–oxygen reaction. The photolysis flash was operated with an energy of 250 J and had an effective duration of 100 μsec. Pressures of chlorine dioxide were $\frac{1}{2}$ mm. mercury or less, and the experiments were conducted in the presence of up to half an atmosphere of inert gas (argon, nitrogen or carbon dioxide) in order to reduce the rise in temperature to a few degrees. Plate densities were measured by reference to calibrations made with a neutral step wedge.

It was found that a single flash decomposed about 90 per cent of the chlorine dioxide and that this spectrum was replaced by that of chlorine monoxide, which then decayed slowly in the same manner as had been observed in previous work. Spectra of other chlorine oxides were absent at all times, and microphotometric measurements at 2780 A. established that chlorine trioxide (ClO_3), which has an extinction coefficient of 1,210 at this wave-length[4], could not have been formed in an amount greater than 1 per cent of the total chlorine dioxide decomposed. This is different from the photolysis of chlorine dioxide at normal intensities, where chlorine trioxide is a major product[5], but the difference can be understood in terms of the following competing reactions:

$$O + ClO_2 = ClO_3 \quad (2)$$

$$O + ClO = ClO_2 \quad (3)$$

$$O + O + M = O_2 + M \quad (4)$$

Since the ratio of the concentration of atomic oxygen plus chlorine monoxide to the dioxide is many thousand times greater in the flash experiments, the probability of reaction 2 relative to 3 and 4 will be correspondingly reduced.

The primary photolysis undoubtedly occurs by the process:

$$ClO_2 + h\nu = ClO + O\,; \quad (5)$$

and therefore, if measurements are made before the chlorine monoxide has reacted to form chlorine, the concentration of chlorine monoxide will be given simply by the difference between the corresponding concentration of chlorine dioxide and the concentration originally present. Allowance was made for the chlorine monoxide which had reacted before measurement by carrying out a number of determinations at pressures of chlorine dioxide of 0·1, 0·2 and 0·5 mm. mercury, and extrapolating to zero concentration. The correction was very small, the observed value at the lowest chlorine dioxide pressure being only 4 per cent less than the extrapolated value, while the mean deviation from the mean at a given pressure was 7 per cent. The final value of the extinction coefficient at 2577 A. obtained in this way was 1,190 ± 100 litre mole^{-1} cm.$^{-1}$. Substituting this numerical value into the expression of Porter and Wright, we obtain:

$$k_1\ (20^\circ\ \text{C.}) = 8{\cdot}6 \times 10^7\ \text{litre mole}^{-1}\ \text{sec.}^{-1}.$$

We have also measured the rate constant of removal of chlorine monoxide independently, using the same methods but preparing it by photolysis of chlorine dioxide. The mean value of the bimolecular constant obtained at 20° C. was $5{\cdot}7 \times 10^7$ litre mole^{-1} sec.$^{-1}$. The difference between these two values is probably within the combined errors of the two completely independent determinations, which used different density standards for plate calibration. It follows that chlorine dioxide, like chlorine and oxygen, has no effect on the rate of disappearance of the ClO radical.

It has been pointed out that reaction 1 has a low frequency factor and the reasons for this have already been discussed[3]. It is one of the simplest bimolecular radical reactions for which quantitative rate data and spectroscopic constants are now available for more detailed theoretical treatment.

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[1] Porter, G., *Proc. Roy. Soc.*, A, **200**, 284 (1950).
[2] Porter, G. *Discuss. Farad. Soc.*, **9**, 60 (1950).
[3] Porter, G., and Wright, F. J., *Discuss. Farad. Soc.*, **14**, 23 (1953).
[4] Goodeve, C. F., and Richardson, F. D., *Trans. Farad. Soc.*, **33**, 453 (1937).
[5] Bodenstein, Harteck and Padelt, *Z. anorg. allgem. Chem.*, **147**, 233 (1925).

RESTRICTION OF INFLAMMATORY RESPONSE BY POLYSACCHARIDES

By M. SHILO, B. WOLMAN and SHLOMO HESTRIN

Laboratory of Microbiological Chemistry, Department of Biochemistry, Hebrew University–Hadassah Medical School, Jerusalem

THE suggestion that colloids from the blood plasma may coat the capillary endothelium and that the porosity of the latter may thereby be reduced was advanced more than a decade ago[1]. However, the possibility of utilizing this mechanism as a means of restricting inflammatory response has perhaps not been appreciated clearly. Water-soluble polysaccharides frequently occur on micro-organisms in the form of capsular envelopes. It is relevant to the mechanism of infection and of interest to learn whether such polymers also can act on blood vessels as wall-coating agents. In the experiments described here, we have attempted in particular to ascertain whether neutral and high-molecular bacterial polysaccharides, lævan and dextran, systemically administered, retard escape of blood colloids and cells across the capillary wall at sites of tissue injury.

The influence of the intravenous administration of high-molecular polysaccharide on the capacity for