Table 1. SUMMARY OF THIOL OXIDATIONS IN 25-ML. TETRAMETHYLGUANIDINE AT 23·5°

Thiol	m.moles	Mole % R_2S_2	Reaction time (h)
Butane-1-	9·51	80	19
Benzene	9·78	82	2
*Cyclo*hexane	7·31	72	16
Propane-1-	10·97	82	19
Propane-2-	10·97	82	19
Toluene-*α*-	8·52	12*	43

* Benzyl disulphide is unstable under these conditions.

that tetramethylguanidine (TMG) would be capable of functioning simultaneously as both a solvent and a base for thiol oxidations. This was found to be true.

Thiol oxidations were carried out in a closed system at 23·5° ± 0·2° and 1,300 r.p.m. under a constant oxygen partial pressure of 1 atmosphere[5]. In all reactions 25 ml. of TMG containing 7–11 m.moles of the desired thiol was used. Each reaction was allowed to proceed until the apparent uptake of oxygen was less than 2 ml./h. Disulphides were qualitatively identified by gas chromatography comparison to authentic samples on a 2-ft. silicone rubber column (30 wt. per cent silicone rubber on 'Chromosorb', 0·25 in. diam.) between 75° and 250°. Quantitative results were obtained by potentiometric titration of the unreacted thiol with silver nitrate, reduction of the disulphide to the thiol in a zinc/acetic acid medium, and a second titration with silver nitrate. As shown in Table 1, the yield of disulphide varied from 12–82 per cent for the thiols listed. Minor amounts of other products were formed but no attempt to establish their structure was made.

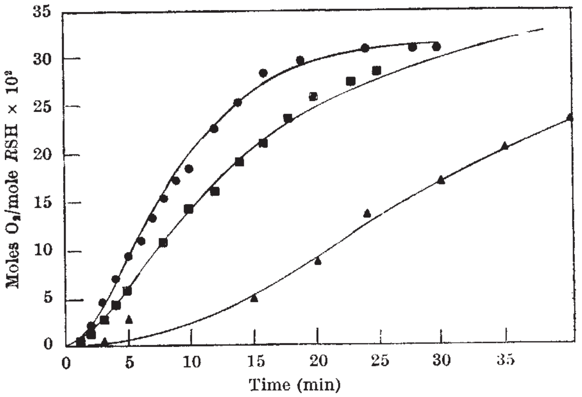

Fig. 1. Typical rates of thiol oxidation in TMG at 23·5°. ●, Benzene; ■, *α*-toluene; ▲, *cyclo*hexane

It should be noted that the foregoing reactions were extremely rapid. Each oxidation was at least 75 per cent complete in 1 h. In contrast to this, it was found that aromatic and aliphatic thiols could not be oxidized in dipolar solvents such as DMAC or DMF at room temperature in the absence of added base. This emphasizes the unique ability of TMG to function as both a base and a solvent. Based on the initial rates of consumption of oxygen, the observed ease of thiol oxidation in TMG was found to be aryl > arakyl > alkyl (Fig. 1). These results suggested that initial ionization of the thiol was rate-determining. This was substantiated by the isolation of several tetramethylguanidinium thiolates from an ethereal solution of TMG (0·1 molar) to which the thiol was added slowly under nitrogen. Benzenethiol, toluene-α-thiol, 4-methylbenzenethiol, 2-methylbenzenethiol, and *p*-xylene, α,α′-dithiol all formed stable adducts with TMG (~ 90 per cent yields) that melted between 80° and 200°. The salts were stable indefinitely when stored under nitrogen but decomposed rapidly to disulphide, water, and TMG when exposed to air. Aliphatic thiols (pK_a 12–14) did not form stable salts with TMG. Thus, for aliphatic thiols, co-oxidation of the unionized thiol and the thiol anion must occur. Since aromatic thiols are much more acidic it would appear that oxidation takes place predominantly by the anion[6].

T. J. WALLACE
N. JACOBSON
A. SCHRIESHEIM

Esso Research and Engineering Co.,
Process Research Division,
Exploratory Research Section,
Linden, New Jersey.

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[1] Gordy, W., and Stanford, S. C., *J. Amer. Chem. Soc.*, **62**, 497 (1940).

[2] Grillot, G. F., and Brooks, J. T., *J. Amer. Chem. Soc.*, **72**, 4281 (1950).

[3] Oswald, A. A., Noel, F., and Stephenson, A. J., *J. Org. Chem.*, **26**, 3969 (1961).

[4] Wallace, T. J., and Schriesheim, A., *Tet. Letters*, No. 17, 1131 (1963).

[5] For a more detailed description of this method, see Wallace, T. J., Bartok, W., and Schriesheim, A., *J. Chem. Educ.*, **40**, 39 (1963).

[6] TMG is an exceptionally strong organic base, and forms very stable salts: *Amer. Cyanamid Co. Bull. IC* 0234-*R*-100-9/60.

Radiation-induced Oxidation of Tetrafluoroethylene by Oxygen

OXIDATION of unsaturated compounds by oxygen has been fully investigated[1–6]. Recently, oxidation of ethylene[7], propylene[8] and tetrachloroethylene[9] has been examined by ionizing radiation. The oxidation of ethylene and propylene leads to the formation of a large number of products and the reported *G* values for the olefine consumption are very low. Tetrachloroethylene is oxidized through a chain mechanism and a *G* value of 910 has been found. Trichloroacetylchloride, phosgene and oxalyl chloride are the main products.

We have found that oxidation of tetrafluoroethylene by oxygen induced by ionizing radiation occurs through a chain reaction leading to the following products: carbonyl fluoride COF_2, tetrafluoroethylene oxide $(CF_2)_2O$ and a liquid polyperoxide.

The irradiation experiments were carried out on 1 : 1 mixtures of tetrafluoroethylene–oxygen at room temperature and at a total pressure of 760 mm mercury. A 6,000-c. cobalt-60 irradiating unit (0·4 Mr./h) and a 50-kV X-ray apparatus (1·55 Mr./h) were the radiation sources.

The reaction products consisted of a gas and of a non-volatile liquid. The gaseous fraction was separated from the liquid and distilled through a Podbielniak column. The low-boiling fraction was COF_2, which has been characterized by the infra-red spectrum[10]. The high-boiling products were $(CF_2)_2O$ and tetrafluoroethylene residual. These products were further fractionated and purified by gas chromatography.

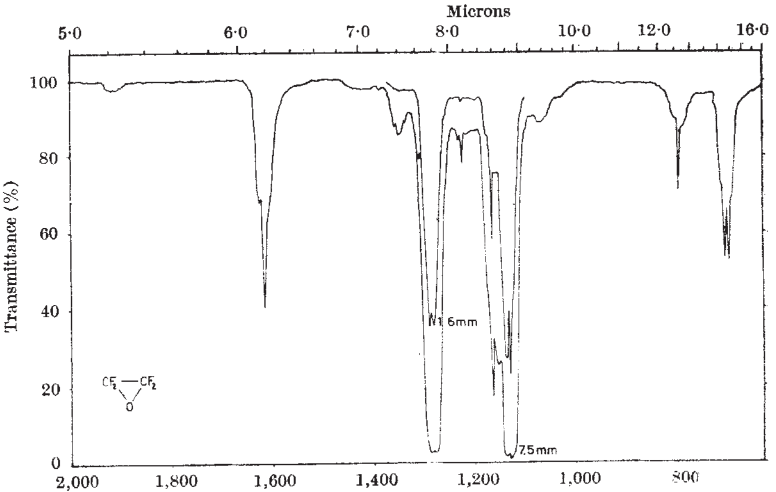

Fig. 1

The purified tetrafluoroethylene oxide has a molecular weight of 115 ± 2. The infra-red spectrum (Fig. 1) does not correspond to trifluoroacetylfluoride and the characteristic band of the carbonyl group at about 5·5μ is absent. The mass spectrum, although it does not show the parent mass at 116 in large amount, indicates the presence of oxygen in the compound and gives fragment masses as would be expected from the chemical formula. The nuclear magnetic resonance spectrum gives a single band at about +3·4δ (trifluoroacetic acid as reference standard). This chemical shift is displaced to a lower field compared with CF_2 groups as would be expected when bound to an oxygen atom.

The elementary analysis of the liquid separated from the volatile gaseous products gave the following results: C, 18·73 per cent; F, 54·04 per cent; O, 26·94 per cent. The nuclear magnetic resonance spectrum shows a major single band at about −23·3δ. The resonance frequency is in a much lower region of the CF_2 group bound to an oxygen atom. This displacement may be in agreement with a polyperoxidic structure of the type:

$$(\text{—}CF_2\text{—}CF_2\text{—}O\text{—}O\text{—})_n$$

the theoretical composition of which is: C, 18·18 per cent; F, 57·57 per cent; O, 24·24 per cent.

Table 1. *G* VALUES CALCULATED FOR THE CONSUMPTION OF OXYGEN AND TETRAFLUOROETHYLENE AND FOR THE FORMATION OF THE REACTION PRODUCTS

The data refer to a 1 : 1 mixture after X-ray irradiation for 30 min at a dose-rate of 1·55 Mr./h

	Moles*	*G*†
C_2F_4	25·0	2,950
O_2	18·3	2,160
COF_2	27·9	3,300
$(CF_3)_2O$	9·2	1,090

* The figures referred to are 100 moles of initial tetrafluoroethylene.

† *G* values refer to molecules consumed or formed per 100 eV absorbed by the mixture.

Table 1 gives the results concerning the irradiation of 1 : 1 mixtures of tetrafluoroethylene and oxygen. As may be observed from the *G* values, the reaction occurs through a chain mechanism.

Discussion of the mechanism which may justify the formation of the various products found will be presented later when more experimental data will be considered.

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V. CAGLIOTI
M. LENZI
A. MELE

Laboratorio di Chimica delle
Radiazioni e Chimica Nucleare,
C.N.E.N.,
Istituto di Chimica Generale,
Università di Roma, Italy.

[1] Myers, R. L., *Indust. Eng. Chem.*, **45**, 1783 (1953).
[2] Miller, jun., W. T., and Dittman, A. L., *J. Amer. Chem. Soc.*, **78**, 2793 (1956).
[3] Frankel, D. M., Jonson, C. E., and Pitt, H. M., *J. Org. Chem.*, **22**, 1119 (1957).
[4] Mayo, F. R., *J. Amer. Chem. Soc.*, **80**, 2465 (1958).
[5] Mayo, F. R., Miller, A. A., and Russell, G. A., *J. Amer. Chem. Soc.*, **80**, 2500 (1958).
[6] Haszeldine, R. N., and Nyman, F., *J. Chem. Soc.*, 1084 (1959).
[7] Michailov, B. M., and Kiselev, V. G., *Isvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1619 (1960).
[8] Mikhailov, B. M., and Kiselev, V. G., *Isvest. Akad. Nauk S.S.S.R. Otdel Khim. Nauk*, 527 (1961).
[9] Sutherland, J. W., and Spinks, J. W. T., *Canad. J. Chem.*, **37**, 79 (1959).
[10] Nielsen, A. H., Burke, T. G., Woltz, P. J. H., and Jones, E. A., *J. Chem. Phys.*, **20**, 596 (1952).

BIOPHYSICS

Equilibrium Temperature of a Small Sphere suspended in Air and exposed to Solar Radiation

FOR small temperature differences between a sphere and its surroundings, heat losses other than those due to conduction can be neglected. Classical theory for the heat loss Q from a sphere per second leads to the formula:

$$Q = 4\pi k(\theta_1 - \theta_0)a$$

where k is the thermal conductivity of the surrounding air, θ_1 and θ_0 are the temperatures of the sphere and the ambient and a is the radius of the sphere. If the sphere is assumed to conduct perfectly and to be exposed to a radiant flux of f cal/cm²/sec, equilibrium will be reached when:

$$4\pi k(\theta_1 - \theta_0)a = \pi a^2 f$$

assuming that all the incident radiation is absorbed by the sphere. The excess temperature of the sphere over its surroundings becomes:

$$(\theta_1 - \theta_0) = \frac{af}{4k}$$

If this result is applied to a sphere of diameter 1μ ($a = \frac{1}{2} \times 10^{-4}$ cm), which is the order of size of airborne bacteria, and f is taken to be 2 cal/cm²/minute (approximately that of solar radiation) and $k = 5{\cdot}74 \times 10^{-5}$ C.G.S. then:

$$(\theta_1 - \theta_0) = \frac{1}{138}\ ^\circ\text{C}$$

Thus an airborne bacterial particle will experience only a very small change in temperature on passing from complete shadow into full sunlight and its temperature will be almost entirely dependent on that of the air surrounding it. Since $(\theta_1 - \theta_0)$ depends linearly on the radius of the particle, even for particles as large as 100μ diameter the temperature change would be less than 1°C.

The assumption that the sphere is perfectly conducting is a reasonable approximation to the case of a bacterial particle. A heat flow of 2 cal/cm²/min passing through a slab of thickness 1μ and having a thermal conductivity equal to that of water would produce a temperature difference of $1{\cdot}9 \times 10^{-3}$ °C between the faces. If allowance is made for heat loss from the hemispherical face of the sphere directed towards the incident radiation a temperature difference of less than 10^{-3} °C between the exposed and non-exposed face can be deduced. A similar calculation for a 100μ particle would predict the temperature difference to be less than 10^{-1} ° C.

It is thought that this deduction, while familiar in principle to cloud physicists, might be of interest to aerobiologists among whom it does not appear to be widely known.

H. A. DRUETT

Microbiological Research Establishment,
Porton, Nr. Salisbury, Wilts.

BIOCHEMISTRY

Fluoro-fatty Acids in the Seeds of *Dichapetalum toxicarium*

IT was reported by Peters, Hall, Ward and Sheppard[1] that the seeds of *Dichapetalum toxicarium* contain at least two fluorinated long-chain fatty acids. The acid present in by far the larger amount was identified as ω-fluoro-oleic acid; but the other acid which is solid at room temperature was not properly identified because of the difficulty of isolating it in a sufficiently pure state.

The purification of this solid fluoro-acid has now been improved. It was first separated from fluoro-oleic acid by freezing, thawing and high-speed centrifuging as already described[1]. The residue was dissolved in 4–5 ml. of acetone and any insoluble material removed by centrifuging. After evaporating off the acetone the residue was redissolved in 5 ml. of light petroleum (b.p. 40°–60° C) and left for several hours at −20° C when the fluoro-fatty acid crystallized out. This was separated by centrifuging and washed with 1 ml. of light petroleum at −20° C. The fluoro-acid was recrystallized twice more in this manner. The final product was a silky white crystalline solid, m.p. 71°–73° C.