ELECTROCHEMICAL REDUCTION OF OZONE ON VARIOUS METALS

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Study of the kinetics and the mechanism of the cathodic reduction of ozone on metals differing in their electrochemical properties can be of definite theoretical and practical interest. Investigation of this process will enable the nature of the electrochemical reduction of oxygen compounds possessing a high oxidation potential to be more fully understood, and the role of ozone in corrosion processes to be clarified.

Little work has been published[1] on the mechanism of the cathodic reduction of ozone in electrochemical systems. A previous paper of ours[2] described an investigation of the electrochemical reduction of ozone at a platinum electrode, suggested a possible mechanism and showed the decisive role of surface compounds of platinum.

The present work extends the study to various metals possessing different electrochemical properties.

EXPERIMENTAL

The electrochemical reduction of ozone has been investigated by cathodic polarography at a fixed electrode in the apparatus illustrated in Fig. 1.

Material was supplied to the electrode by continuous circulation of the electrolyte solution saturated with ozone to a definite concentration. The rate of rotation of the magnetic stirrer was determined by means of a stroboscopic revolution counter.

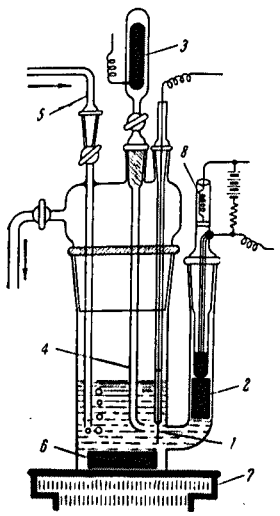

Fig. 1. Polarographic cell: 1) test electrode; 2) unpolarisable electrode; 3) reference electrode; 4) electrolytic bridge; 5) gas inlet tube; 6) magnetic core in glass sheath; 7) magnetic stirrer.

The acid used in the experiments was purified by threefold distillation and its solutions were made up with twice-distilled water.

The electrode was a wire of diameter 0.3 or 1 mm and with an apparent surface varying between 0.05 and 0.15 cm^2. Before each experiment the electrode was boiled in concentrated nitric acid for 30 min, and then thoroughly washed in boiling twice-distilled water. The polarograph was a specially adapted electronic potentiometer of type EPP-09, the great advantage of which was that it incorporated a pen recorder. This instrument enabled the rate of polarisation $\Delta v/\Delta t$ to be varied between 0.25 and 100 mV sec^{-1}, the limits set by the reduction gear.

The volume of electrolyte solution did not exceed 25 ml. The ozone was prepared by the method described in ref. 2. In each experiment polarograms were generally obtained from 1.80 V up to the potential for hydrogen evolution, and in the opposite direction. For convenience, polarograms obtained in this way will henceforward be termed forward and reverse curves respectively.

All potentials quoted in the text are referred to that of the hydrogen electrode in the same solution.

Cathodic Reduction of Ozone at a Gold Electrode

Gold has been the subject of several detailed and comprehensive electrochemical studies[3]. It was found that surface oxygen compounds are formed on the electrode during anodic polarisation, in which the oxygen has variable activity and its bonding to the metal is of variable strength.

The interaction of ozone with gold in electrolyte solutions must apparently be regarded as anodic polarisation of the gold electrode to a potential corresponding to the ozone electrode.[8] It is therefore clear why oxygen surface compounds of gold, capable of existing within this potential range, are formed on the electrode. The cathodic reduction of ozone at a gold electrode at 25° must thus be inevitably linked in some way with the chemisorption of ozone and its decomposition products on the electrode surface. Consequently, the kinetics and mechanism of the electrochemical reduction of ozone should be determined by the electrochemical properties of the resulting surface compounds of the metal with oxygen.

Our hypotheses as to the mechanism of the cathodic reduction of ozone are evidently valid only for the potential range under investigation. At more cathodic potentials, with hydrogen overpotential, electrochemical reduction of ozone may take place by a different mechanism.

Fig. 2 shows cathodic polarograms for the reduction of ozone in 10 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°, the solution being agitated by the magnetic stirrer. The polarogram has two waves representing the reduction of ozone and oxygen respectively. The ozone waves on the forward and reverse curves have $\varphi_{\frac{1}{2}}$ = 1.18 and 1.44 V respectively, the corresponding values for the oxygen waves being 0.47 and 0.54 V. The limiting diffusion current for the first wave varies linearly with the concentration of ozone in the solution, and hence with its concentration in the gas, since the solubility of ozone is known to obey

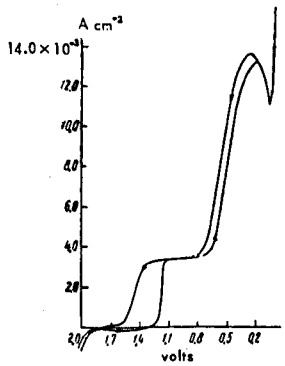

Fig. 2. Cathodic polarograms obtained at a gold electrode in 10 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. Rate of polarisation 2.5 mV sec^{-1}. Rate of rotation of magnetic stirrer m = 1000 rev min^{-1}.

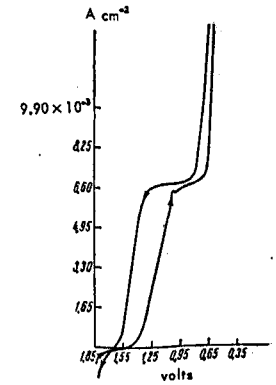

Fig. 3. Cathodic polarograms obtained at a gold electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. Rate of polarisation 10 mV sec^{-1}. Rate of rotation of magnetic stirrer m = 1000 rev min^{-1}.

Henry's law.[4] The slope $\partial\varphi/\partial \log i$ of the linear portion of the ozone and oxygen waves is about 750 mV and above.

Hysteresis is more marked with the ozone than with the oxygen waves. If the electrode is kept for a short while near the hydrogen potential, both waves are shifted to more positive potentials. Reduction then appears to take place with a smaller energy of activation, *i.e.* with a lower overpotential.

The limiting diffusion current i_d on the forward and reverse curves is the same, its value being 10.2×10^{-3} and 3.42×10^{-3} A cm^{-2} for oxygen and ozone respectively. All calculations of current density are based on unit apparent surface.

The experiments showed that a 35-fold change in the rate of polarisation had no effect on the character of the reduction of ozone, the parameters of the polarogram being the same, for example, at polarisation rates of 86 and 2.5 mV sec^{-1}.

Fig. 3 shows polarograms for the cathodic reduction of ozone at a gold electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. The tenfold change in acid concentration has had practically no effect on the character of the cathodic reduction of ozone and oxygen. Here there has been only an increase in the limiting diffusion current, approximately by a factor of two, caused by the increased solubility of ozone[4] and the increase in the rate of diffusion of ozone and oxygen.

As was to be expected, the cathodic reduction of ozone in 0.2 N KOH differs from that in acid. The polarogram now has only one wave with $\varphi_{\frac{1}{2}}$ = 0.60 and 0.70 mV for the forward and reverse curves respectively. This wave apparently corresponds to the reduction of oxygen, since ozone is known to decompose rapidly in alkaline solutions.

Cathodic Reduction of Ozone at a Palladium Electrode

The electrochemical properties of a palladium electrode have been quite thoroughly investigated as regards cathodic processes[6], a number of interesting reactions having been obtained for the electrochemical interaction between this metal and hydrogen, leading to the formation of the hydrogen compounds of palladium which govern the cathodic behaviour of this electrode.

Both our own and published results show that palladium is a good electrochemical adsorbent of hydrogen and oxygen, surface or bulk compounds being formed which, as we shall see later, are of importance.

Fig. 4 shows polarograms for the cathodic reduction of ozone and oxygen at a palladium electrode in 1 N H_2SO_4 solution saturated with ozone (30%) and oxygen (70%) at 25°.

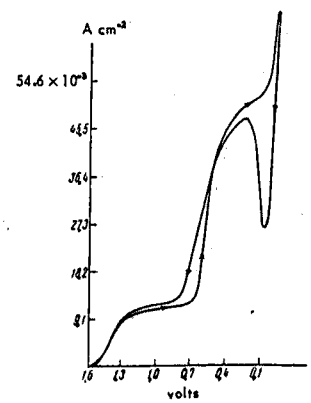

Fig. 4. Cathodic polarograms obtained at a palladium electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. Rate of polarisation 10 mV sec^{-1}. Rate of rotation of magnetic stirrer m = 1000 rev min^{-1}.

The curves have two waves representing the reduction of ozone and oxygen. Hysteresis between forward and reverse polarograms is much less marked with a palladium electrode than with platinum or gold, the ozone and oxygen waves coinciding on the forward and reverse curves [?(Ed. of Translation)].

The half-wave potential for the reduction of ozone on palladium is 1.42 V, the corresponding values for oxygen being 0.58 and 0.62 V for the forward and reverse curves respectively. The limiting diffusion currents for the reduction of ozone and oxygen are 10.9×10^{-3} and 34.6×10^{-3} A cm^{-2} respectively. The slope $\partial\varphi/\partial \log i$ of the linear part of the ozone reduction wave at a palladium electrode is about 30–50% of that at platinum and gold, its value being 400 mV.

The reverse polarogram for the cathodic reduction of ozone on palladium at first differs considerably from the forward curve (see Fig.4). After the electrode has remained for a short time in the vicinity of the hydrogen electrode potential it becomes passive and remains so while reduction of ozone takes place over the range 0–0.30 V. The passivation is particularly evident at a palladium electrode. This phenomenon occurs to a lesser extent on platinum and gold. The quantity of adsorbed hydrogen which can accumulate on a palladium electrode may be such that the reverse polarogram does not reproduce the forward curve. If, for example, a palladium electrode is kept at 0.05 V for 5 min, the initial part of the reverse polarogram, from 0.05 to 0.20 V, shows that the current has fallen to zero and below, having changed its direction, and then from close to 0.40 V the curve continues as far as 1.55 V at $i_d = 0$. Consequently, electrochemical reduction of ozone and oxygen does not occur in this case. It must be assumed that under these conditions the normal chemical reaction between ozone and the hydrogen adsorbed on the electrode takes place on the surface of the metal by a catalytic mechanism. This process continues until all the hydrogen has been used up.

In this work we are, of course, interested in the nature and degree of oxidation of palladium by ozone in sulphuric acid solution. Experiments carried out in 0.1 N and 1.0 N H_2SO_4 show that oxides having identical properties are produced on palladium whether it is oxidised electrochemically or with ozone.

The charging curves for cathodic reduction obtained with electrodes which have been oxidised either with ozone or electrochemically in 0.2 N H_2SO_4 have two almost horizontal arrests, one at 0.75–0.80 V, and the other at 1.35–1.40 V. The amount of oxygen in these surface or bulk compounds can vary with the conditions of oxidation, the bulk oxides apparently being compounds of the type PdO_2 and PdO_3.

Palladium trioxide is a very strong oxidant in acid solutions.[8] The potential of the PdO–PdO_2 system is 0.95 V according to Jirsa[10], who also determined the potential of the reaction

$$PdO_3 + H_2O + 2e = PdO_2 + 2OH^-, \quad E^\circ = 1.2 \text{ V}$$

The potentials given for these reactions are quite close to those for the oxides formed on a palladium electrode, either by ozone or electrochemically. This agreement is evidently not fortuitous.

Comparison of the electrochemical characteristics obtained for the cathodic reduction of ozone at a palladium electrode with results obtained in the cathodic reduction of oxygen compounds which were formed on palladium either chemically or electrochemically shows a definite connection between these processes.

Cathodic Reduction of Ozone and Oxygen at Tungsten and Tantalum Electrodes

Tungsten and tantalum are of interest because the oxygen atoms chemisorbed on their surfaces have a particularly profound effect on their electrochemical properties. On anodic polarisation in acid solutions, these metals form oxide layers possessing clearly defined semiconductor properties. Such oxides possess unipolar conduction; a characteristic feature is that under normal conditions they are not reduced electrochemically, which is evidence of the great strength of the metal–oxygen bond.

Our view that electrochemical reduction of ozone and oxygen at potentials between 0 and 1.80 V involves oxygen surface compounds of the electrode, with a labile metal–oxygen bond (so that they are electrochemically active), has been confirmed for such metals as platinium, gold, palladium, iridium, and rhodium. According to our view, reduction of oxygen and ozone cannot take place at tungsten and tantalum electrodes, because these metals form surface oxides in which the metal–oxygen bond is very strong, so that they are electrochemically inactive under normal conditions. In order to confirm this, experiments were carried out on the cathodic reduction of ozone and oxygen at tungsten and tantalum electrodes.

Fig.5 shows forward and reverse cathodic polarograms obtained at a tantalum electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%). The absence of waves is a sure indication that ozone and oxygen are not reduced at a tantalum electrode. The same type of polarogram is obtained with oxygen alone.

A similar polarogram to that illustrated in Fig.5 is obtained when an attempt is made to reduce oxygen at a tungsten electrode. Hence reduction of oxygen does not take place at a tungsten electrode either.

It might be thought that no process at all is possible within this range of potentials at such electrodes, since the

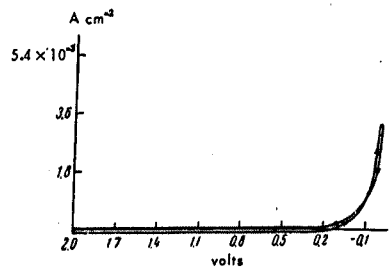

Fig. 5. Cathodic polarograms for ozone at a tantalum electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. Rate of polarisation 10 mV sec^{-1}. Rate of rotation of magnetic stirrer m = 1000 rev min^{-1}.

electrode is covered with an insulating oxide film. However, this is not the case. If, for example, the reduction of ferric to ferrous iron, or the reverse oxidation, is carried out at such an electrode, the polarograms show distinct waves corresponding to these processes. The half-wave potentials determined from the polarograms for the process $Fe^{2+} - e \rightleftharpoons Fe^{3+}$ are exactly 0.77 V, the same as the value obtained from thermodynamic data and determined experimentally at other electrodes.

Consequently, if an electrochemical reduction or oxidation is not complicated by other stages and the complete process is merely a simple electron transfer, the process can take place at such an electrode. When the electrochemical reduction or oxidation is associated with a transfer to matter involving the reactant species, the governing factor in the electrochemical process will be the surface compounds of the electrode and their properties.

Fig. 6 shows polarograms for the cathodic reduction of ozone at a tungsten electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. The polarograms show a wave corresponding to the reduction of ozone. Hysteresis is observed between the forward and reverse curves, the respective half-wave potentials being 0.30 and 0.70 V. This shift in the waves is due to the different initial conditions of the electrode surface.

The electrode was maintained at a potential of 2.00 V for 5 min before the recording of the forward curve, and at -0.20 V for some time before the reverse curve was recorded. Thus in the former case the polarogram was obtained at an oxidised electrode, and in the latter at an electrode whose surface had been to some extent reduced.

The slope $\partial\varphi/\partial \log i$ of the linear part of the ozone reduction wave is 505 mV. If polarograms for the reduction of ozone at a tungsten electrode are recorded between 1.50 and 1.30 V, the forward and reverse curves coincide, the half-wave potential being 0.70 V. Maintaining the tungsten electrode at 2.00 V and above brings it to a passive condition, and therefore the process is accompanied by a considerable overpotential, $\varphi_{\frac{1}{2}} = 0.30$ V. There is hysteresis, because the electrode is in different initial states for forward and reverse curves.

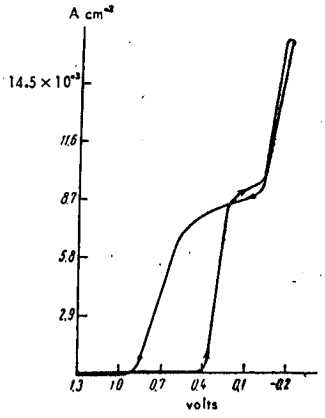

Fig. 6. Cathodic polarograms obtained at a tungsten electrode in 1 N H_2SO_4 saturated with ozone (30%) and oxygen (70%) at 25°. Rate of polarisation 10 mV sec^{-1}. Rate of rotation of magnetic stirrer m = 1000 rev min^{-1}.

DISCUSSION

The experimental results obtained for the cathodic reduction of ozone and oxygen at different metals indicate its complicated character. The Table gives the half-wave potentials and the slopes $\partial\varphi/\partial \log i$ of the linear part of the ozone reduction wave, determined from the forward and reverse polarograms obtained with various metals in 1 N H_2SO_4 at 25°.

It has been shown[2] that the cathodic reduction of ozone at a platinum electrode at 25° is irreversible. The value of $\varphi_{\frac{1}{2}}$ cited above cannot, of course, be identified with the value for the reversible process. We believe, however, that it can be a quite definite characteristic of the irreversible process. All the experimental results show that the half-wave potential for the reduction of ozone must be associated with the formation of surface compounds of the electrode, which are rapidly produced by reaction with ozone[7].

It is readily seen that the potentials for the cathodic reduction of the oxygen compounds on platinum[5a-5c], gold[3], palladium, and rhodium[9] are equal to the half-wave potentials for the cathodic reduction of ozone on the same metals. This coincidence is evidently not fortuitous.

The values listed in the Table for $\varphi_{\frac{1}{2}}$ for the cathodic reduction of ozone on various metals indicate that this process is definitely affected by the nature of the metal, depending on the electrochemical properties of the surface oxygen compounds of the metal, mainly on the strength of the metal–oxygen bond. This point is particularly clearly illustrated by the experiments with a tantalum electrode, at which the cathodic reduction does not take place. Within this range of potentials oxides are known to be present on its surface in which the oxygen is firmly bound to the metal, so that tantalum is passive.

A characteristic feature of the cathodic reduction of ozone on all the metals which we have investigated is the steep slope $\partial\varphi/\partial \log i$ of the linear part of the polarographic wave (see Table). The slope of the wave increases with a rise in the acid concentration. Thus in 10 N H_2SO_4, for example, the values at a platinum electrode are 1400 and

TABLE.

Metal	Half-wave potential $\varphi_{\frac{1}{2}}$, V		Slope $\partial\varphi/\partial \log i$, mV
	forward curve	reverse curve	
Platinum	1.22	1.36	750—800
Gold	1.20	1.45	600—650
Palladium	1.42	1.42	400
Iridium	0.85	1.06	650—810
Rhodium	1.07	1.20	665—700
Tungsten	0.30	0.70	505
Tantalum	no wave		

2200 mV for the forward and reverse polarograms respectively. The exceptionally high value of $\partial\varphi/\partial \log i$ indicates that α, which in the kinetic equation represents the efficiency with which the electric field acts on the ion undergoing discharge, is very small. Consequently, a considerable part of the effect of the electric field will be concentrated on the chemisorbed surface compound of oxygen.

It follows from our experimental results that the absence of chemisorbed oxygen from the surface produces an abrupt change in the electrochemical kinetics, as is shown particularly clearly at a palladium electrode, which adsorbs hydrogen very well.

The hysteresis observed in our experiments must evidently be ascribed to the participation of surface oxygen compounds, and is mainly due to the fact[5a–5b] that the electrochemical adsorption of oxygen on a metal surface involves the so-called "strengthening" of the metal–oxygen bond.

When all the experimental results obtained on the cathodic reduction of ozone are assembled and analysed, we can represent this process at 25° by the general equations

$$MO + O_3 = MO(O)_{ads} + O_2,$$
$$MO(O)_{ads} + 2H^+ + 2\overset{\ominus}{e} = MO + H_2O,$$

where $MO(O)_{ads}$ denotes the higher oxygen compound formed at the potential of the ozone electrode (E° = 2.07 V).[6]

The experimental results reported in this and previous[2] papers demonstrate that the electrochemical reduction of ozone at a metal electrode at 25° and potentials between 1.80 V and that of the hydrogen electrode must of necessity pass through a stage involving the chemisorption of the ozone on the metal surface. The active surface compounds which are thus formed govern the kinetics and mechanism of the cathodic process.

We therefore consider that a theoretical interpretation of the cathodic reduction of ozone, and apparently of oxygen compounds possessing a high oxidising potential, is impossible without taking into account the state of the electrode surface and the properties of the surface compounds which are formed on it.

SUMMARY

1. An investigation has been made of the cathodic reduction of ozone on various metals (gold, palladium, rhodium, iridium, tungsten, and tantalum) at potentials between 1.80 V and that of the hydrogen electrode in sulphuric acid solutions at 25°.
2. The electrochemical reduction of ozone depends on the nature of the metal and the state of the electrode surface. The role of adsorbed oxygen in the cathodic process has been determined.
3. A possible mechanism is suggested for the cathodic reduction of ozone in which the rate-determining stage is assumed to be the formation and reduction of surface compounds of the electrode with oxygen.

1. N. A. Tomashov and Z. A. Valiulina, Zhur. Fiz. Khim., 26, 417 (1952).
2. K. I. Nosova, A. A. Rakov, and V. I. Veselovskii, Zhur. Fiz. Khim., 33, 549 (1959) [Russ. J. Phys. Chem., Abs., 12 (1959)].
3. W. J. Shutt and A. Walton, Trans. Faraday Soc., 28, 740 (1932); Parsons and Butler, Trans. Faraday Soc., 28, 471 (1932); W. J. Shutt and A. Walton, Trans. Faraday Soc., 29, 1209 (1933); W. J. Shutt and A. Walton, Trans. Faraday Soc., 30, 915 (1934); G. Armstrong and J. A. V. Butler, Trans. Faraday Soc., 30, 1173 (1934); W. J. Shutt and A. Walton, Trans. Faraday Soc., 31, 636 (1935); G. Armstrong and J. A. V. Butler, Proc. Roy. Soc., 143, 89 (1934); D. Clark, T. Dickinson, and W. N. Mair, Trans. Faraday Soc., 55, 1937 (1959); N. A. Fedotov, Thesis, Karpov Physicochemical Institute, 1940; G. A. Deborin and B. V. Ershler, Zhur. Fiz. Khim., 14, 708 (1940); V. I. Veselovskii, Zhur. Fiz. Khim., 20, 269 (1946); K. A. Lapteva, T. I. Borisova, and G. N. Slin'ko, Zhur. Fiz. Khim., 30, 61 (1956).
4. L. I. Kashtanov and O. N. Oleshuk, Zhur. Obshch. Khim., 7, 839 (1937).
5. *a*) Ts. I. Zalkind and B. V. Ershler, Zhur. Fiz. Khim., 25, 566 (1951); *b*) V. I. Nesterova and A. N. Frumkin, Zhur. Fiz. Khim., 26, 1178 (1952); *c*) A. D. Obrucheva, Zhur. Fiz. Khim., 26, 1472 (1952); *d*) T. I. Borisova and V. I. Veselovskii, Zhur. Fiz. Khim., 27, 1195 (1953); *e*) K. I. Rozental' and V. I. Veselovskii, Dokl. Akad. Nauk SSSR, 111, 637 (1956).
6. A. N. Frumkin and N. A. Aladzhalova, Zhur. Fiz. Khim., 18, 493 (1944); A. I. Fedorova and A. N. Frumkin, Zhur. Fiz. Khim., 27, 247, 516 (1953).
7. L. Tronstad and T. Höverstad, Trans. Faraday Soc., 30, 1114 (1934); T. N. Krylova, Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk, No. 10, 189 (1938).
8. W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Solution" (Translated into Russian), 1954, p. 48.
9. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), 1952, p. 53.
10. F. Jirsa, Z. phys. Chem., 113, 241 (1924).

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THE RELATIVE REACTIVITY OF VINYL MONOMERS TOWARDS THE BENZOYLOXY RADICAL

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One of the authors in collaboration with Milyutinskaya[1] has suggested a method of determining the relative reactivity of vinyl monomers towards the benzoyloxy radical, based on the readiness of benzoyloxy radicals to eliminate a molecule of carbon dioxide and form a phenyl radical:

$$PhCOO^\cdot \rightarrow Ph^\cdot + CO_2. \quad (1)$$

In the presence of a monomer the concurrent addition of the benzoyloxy radical to the double bond occurs:

$$PhCOO^\cdot + M \rightarrow PhCOOM^\cdot. \quad (2)$$