Heidelberger and Dan Campbell for advice and assistance.

Summary

It is assumed that antibodies differ from normal serum globulin only in the way in which the two end parts of the globulin polypeptide chain are coiled, these parts, as a result of their amino-acid composition and order, having accessible a very great many configurations with nearly the same stability; under the influence of an antigen molecule they assume configurations complementary to surface regions of the antigen, thus forming two active ends. After the freeing of one end and the liberation of the central part of the chain this part of the chain folds up to form the central part of the antibody molecule, with two oppositely-directed ends able to attach themselves to two antigen molecules.

Among the points of comparison of the theory and experiment are the following: the heterogeneity of sera, the bivalence of antibodies and multivalence of antigens, the framework structure and molecular ratio of antibody–antigen precipitates, the use of a single antigen molecule as template for an antibody molecule, criteria for antigenic activity, the behavior of antigens containing two different haptens, the antigenic activity of antibodies, factors affecting the rate of antibody production and the specificity of antibodies, and the effect of denaturing agents. It is shown that most of the reported experimental results are compatible with the theory. Some new experiments suggested by the theory are mentioned.

PASADENA, CALIFORNIA RECEIVED JUNE 25, 1940

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Thermal Decomposition of Benzoyl Peroxide

BY DENTON JACOBS BROWN

In a recent article, Walker and Wild[1] accept the idea that the acyl peroxide decomposes directly to the dialkyl and carbon dioxide, or reacts with other substances. The object of this work was to make a series of determinations of the rate of decomposition of benzoyl peroxide in order to secure a better insight into the mechanism of the reaction.

Calculated amounts of benzoyl peroxide were diluted with dried benzene to a definite volume in a platinum still or Kjeldahl flask or bomb tubes and placed in a thermostat kept at 80 ± 0.1°. At definite intervals samples were removed, cooled quickly to 20° and a measured portion titrated iodometrically for the undecomposed peroxide. In case of the small bomb tubes, to test the effect of surface, the volume was measured when the original portion was added to the tube.

In the observations for the initial changes of concentration, sufficient benzoyl peroxide was added to the hot benzene in the platinum still so that when all had dissolved the temperature was 80 ± 0.5°. For an example we have included a concentration equivalent to that of tenth molar at 20°. The first portion, 10 ml., was measured hot as soon as the peroxide had dissolved. Of course if a median time were used the initial change for fifteen minutes would be less.

TABLE I

		$(C - x)$ cc.	0.956 $N/10$	$Na_2S_2O_3$
t, min.	A	B	C	D
0	19.55	20.10	20.45	20.10
15	19.20	19.80	20.15	19.70
30	18.60	19.10	19.45	18.95
45	17.95	18.30	18.80	18.40
60	17.25	17.60	18.20	17.85

Following this "induction period" a series of observations were made to determine the order of the reaction.

The data for the least concentrated solutions were the least accurate. For this reason we will include two parallel series for the most dilute

TABLE II

t, min.	$C-x$ (a)	(b)	C_c	K_1	K_2
30	0.0236	0.0230	(0.0233)		
90	.0214	.0208	.0211	0.00165	0.0730
150	.0194	.0195	.0193	163	768
210	.0175	.0175	.0175	166	831
270	.0155		.0159	175	929
300		.0150	.0152		
360	.0142		.0138	154	853
390		.0129	.0132		
450	.0135		.0120	133	760
480		.0122	.0116		

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[1] Walker and Wild, *J. Chem. Soc.*, 1132 (1937).

solutions studied. K_1 and K_2, first and second order "constants," are for series (a). C_c is the calculated concentration using the equation $C_c = 0.30C_1/[(0.30 + C_1)e^{-.00150\Delta t} - C_1]$ for the initial concentration of (0.0233).

The following determinations (Table III) are representative of the other observations. K_1 and K_2 are calculated for series (a).

TABLE III

t, min.	$C-x$ (a)	(b)	C_c	K_1	K_2
30	0.0464	0.0460	(0.0462)		
60	440	437	.0439	0.00180	0.0392
90	419	415	.0414	172	386
120	395	397	.0397	178	418
150	376	373	.0377	176	432
210	348	344	.0341	160	399
270	314	316	.0309	163	421
330	298	293	.0280	148	400
390	274	265	.0254	146	415
450	248	247	.0231	149	447
510	228	233	.0210	148	464

The benzoyl peroxide in xylene solution gave first order constants of the same relation as found by Walker and Wild. Peroxides oxidize the side chains of the aromatic nucleus quite rapidly, but oxidize benzene exceedingly slowly.

The order of the reaction was calculated using the Noyes formula

$$n = 1 + \frac{\log \Delta t'' - \log \Delta t'}{\log C' - \log C''}$$

The values for C are actual values after the induction period and Δt the time for a third decomposition. The most concentrated solution is considered as C'.

TABLE IV

Δt, min.	C	n
110	0.5900	
130	.3527	1.32
165	.1833	1.35
200	.0874	1.31
240	.0464	1.31
260	.0230	1.25

The averages of the calculated constants using the integrated form of the equation for two parallel reactions or autocatalysis

$$-\mathrm{d}c/\mathrm{d}t = K'C + K''C^2$$

were $K' = 0.00150$, $K'' = 0.0050$ and $K'/K'' = 0.30$. These values are used in the recalculated integrated form above

$$C_c = \frac{0.30C_1}{(0.30 + C_1)e^{-0.00150(t_2-t_1)} - C_1}$$

The surface effect was determined by adding 116 sq. cm. of platinum foil to the platinum still, thus tripling the surface.

TABLE V

t, min.	$C - x$	C_c
15	0.0963	(0.0963)
45	.0899	.0908
75	.0851	.0857
105	.0803	.0809
165	.0724	.0723
255	.0610	.0614
375	.0473	.0496

This is a marked contrast to hydrogen peroxide for which we were not able to find any surface that did not catalyze the reaction.

Two parallel series were made in light in a Kjeldahl flask (a) and "bomb" tubes (b), thus determining the effect of surface as well as light.

TABLE VI

t, min.	(a) $C - x$	K_1	(b) $C - x$	K_1
30	0.3693		0.3553	
120	.2642	0.00371	.2512	0.00386
210	.1926	.00362	.1833	.00368
330	.1265	.00357	.1181	.00367
450	.0838	.00348	.0828	.00348

TABLE VII

t, min.	(a) $C - x$	K_1	(b) $C - x$	K_1
30	0.1888		0.1823	
60	.1723	0.00306	.1663	0.00302
120	.1446	.00297	.1395	.00297
180	.1288	.00287	.1163	.00299
240	.1051	.00278	.0977	.00297
360	.0790	.00264	.0700	.00290

From values in Tables VI and VII the calculated order of the reaction is 1.33, while K_1 and K_2 are decidedly greater in presence of light.

When the decomposition of the benzoyl peroxide was observed in an atmosphere of carbon dioxide, no oxygen was detected in the evolved gas.

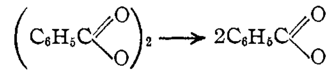
For the analysis of the decomposition products, 0.1 and 0.8 M solutions were decomposed almost completely, but in terms of the order of the reaction to approximately the same degree. The following were determined.

TABLE VIII

	0.1 M	0.8 M
Carbon dioxide	20.2%	12.3%
Diphenyl	27.7	15.1
Phenol	Trace	0.03
Benzoic acid	23.9	35.5
Residue	26.2	37.7

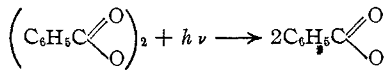
In general our results are as follows: the velocity of decomposition of the benzoyl peroxide dissolved in benzene begins at zero, rises to a maximum in a short interval of time, and then satisfies the conditions for parallel monomolecular and dimolecular reactions. Light accelerates but does not change the order of the reaction. Change of surface area has no effect. Diphenyl and carbon dioxide are the products of the monomolecular reaction and benzoic acid and the residue of the dimolecular reaction.

The gradual increase of velocity, Table I, may be represented as an initial thermal dissociation



$$\left(C_6H_5C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)_2 \longrightarrow 2C_6H_5C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$$

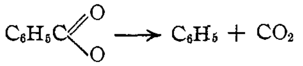
If benzoyl peroxide were the reactant, we would not expect this acceleration. Since light accelerates the rate of reaction but does not change the order, Tables VI and VII, this may be represented thus



$$\left(C_6H_5C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)_2 + h\nu \longrightarrow 2C_6H_5C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$$

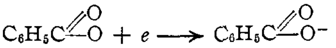
as suggested by Walker and Wild.

Following the dissociation we have parallel first and second order reactions. The first order reaction may be due to the decomposition of the radical



$$C_6H_5C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix} \longrightarrow C_6H_5 + CO_2$$

The parallel second order reaction may be the reaction of the peroxide radical as an oxidizer to form benzoate



$$C_6H_5C\overset{\diagup\!\!\diagup O}{-}O + e \longrightarrow C_6H_5C\overset{\diagup\!\!\diagup O}{-}O^-$$

These parallel reactions are indicated by the increase in fraction of benzoic acid and decrease of diphenyl and carbon dioxide formed in the more concentrated solutions.

Summary

We have observed the initial velocities for concentrations of the range of 0.80 to 0.025 molar benzoyl peroxide in benzene, determined the rate of decomposition, the effects of surface and light, made partial analyses of the products and advanced an interpretation of the results.

LINCOLN, NEBRASKA RECEIVED FEBRUARY 12, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cyclization of Dienynes. VIII.[1] Ring Closures with Alpha and Beta Cyclohexenylacetylene Derivatives of Octalin

BY C. S. MARVEL, D. E. PEARSON AND L. A. PATTERSON

The cyclization reaction which occurs when substituted dienynes are treated with sulfuric acid has now been extended to some alpha and beta derivatives of octahydronaphthalene. The resulting cyclic ketones have been characterized by reduction to cyclic hydrocarbons and dehydrogenation to yield chrysene, 1,2-benzanthracene and picene.

A mixture of *cis*- and *trans*-1-decalone (I) was converted to the ethynyl carbinol (II) by treatment with potassium *t*-amylate and acetylene[2] and the acetylenic carbinol was treated successively with ethylmagnesium bromide and cyclohexanone to yield the acetylenic glycol (III). Dehydration of this glycol gave the dienyne (IV) which was readily cyclized by sulfuric acid to give a mixture of products from which the hexadecahydrochrysenone (V) was isolated.

The structure of this cyclic ketone was established by the following facts. A modified Clemmensen reduction[3] gives an unsaturated hydrocarbon which is readily dehydrogenated over platinum[4] to give chrysene (VI) in excellent yield. The ketone also yields chrysene when heated with platinum catalyst. The unsaturated ketone was reduced to a saturated alcohol (VII), reoxidized to a ketone (VIII) and treated with methylmagnesium iodide to give a carbinol (IX) which on dehydrogenation gave 6-methylchrysene (X).

The position of the carbon–carbon double bond in the cyclization product (V) is still somewhat uncertain. Linstead and Walpole[5] have shown that in the analogous ring closure which leads to a phenanthrone derivative, the double union in the cyclic ketone is conjugated with the car-

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[1] For the seventh communication on this topic see THIS JOURNAL, **61**, 2003 (1939).

[2] Compare Gould and Thompson, *ibid.*, **57**, 340 (1935).

[3] Martin, *ibid.*, **58**, 1438 (1936).

[4] Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).

[5] Linstead and Walpole, *ibid.*, 842 (1939).