[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Recoil Reactions with High Intensity Slow Neutron Sources. I.[1] The Szilard–Chalmers Enrichment of 35.9 h Br^{82}

BY G. E. BOYD, J. W. COBBLE AND SOL WEXLER[2]

Enriched 35.9 h Br^{82} samples from a Szilard–Chalmers reaction in crystalline $KBrO_3$ (in the Oak Ridge graphite pile) showed specific activities up to 750 rd./mg., corresponding to a 22,000-fold enrichment. The variation of the specific activity with irradiation time and neutron source intensity agreed with an elementary theory based on the activation equation and the assumption that the rate of the non-activating radiation decomposition was proportional to the mass irradiated and to the intensity. The prediction that the *specific activity* will be independent of the source intensity and will decrease with increasing time was confirmed as was the predicted inverse dependence of the *enrichment* on source strength and time. The retention of radiobromine as bromate was found to increase with time suggesting a radiation recombination may occur.

Introduction

The recoil effect following the capture of slow neutrons by atomic nuclei has been known almost from the time of the discovery of artificial radioactivity. Since its demonstration by Szilard and Chalmers,[3] numerous investigators have employed the reaction to prepare sources of undetermined high specific activity, or to produce recoil atoms possessing unusual chemical reactivities. There have been, however, virtually no quantitative studies of the total changes in compounds in which the recoiling radioatoms are formed. Gamma rays and fast neutrons always present in slow neutron sources regardless of how they are sustained also act to rupture chemical bonds. Non-radioactive isotopes are released which dilute the active species and lower the specific activity. The radiation decomposition fragments which are many orders of magnitude more numerous than the recoiled radioatoms may also react with the latter and reduce the yield of separable radioactivity appreciably. Very little attention has been given by workers in the field of "hot atom" chemistry to this possible complication.

The past neglect of radiation decomposition effects has resulted from the limitations of conventional analytical methods for the estimation of the ultramicro amounts formed by weak neutron sources. The availability of modern high intensity slow neutron sources, such as the chain reacting pile, has permitted a re-examination of this aspect, since there has been a proportionately increased radiation decomposition to levels accurately determinable by microchemical techniques. A further advantage over radium–beryllium and cyclotron sustained neutron sources is that the intensity may be varied over wide ranges, making it convenient to determine the effects of source strength.

Carefully purified crystalline potassium bromate was employed in this study of the formation of chemically separable 35.9 h Br^{82}. Measurements of the inactive bromine simultaneously produced by radiation decomposition were made so that the variation of the specific activity and degree of enrichment of the recoiled radiobromine could be compared with the predictions from a simple theory. A comparison of a limited amount of semi-quantitative data on other compounds with this theory has been published elsewhere.[4]

Experimental Procedures

Commercial C.P. potassium bromate which ordinarily contains 200–1000 p.p.m. of bromide was unsatisfactory since many of the specific activity determinations in this work involved only a few hundred p.p.m. Approximately 400 g. of bromate was purified in batches as follows: About 40 g. of Baker Analyzed $KBrO_3$ was dissolved in 800 ml. of distilled water, cooled to 10°, and gaseous chlorine passed through for two hours. The treated solution was filtered and extracted with reagent grade carbon tetrachloride until it was colorless and odorless. After three more extractions, the aqueous phase was evaporated to about one-half its volume and cooled slowly to *ca.* 10°. The crystallized $KBrO_3$ was separated, washed with 95% alcohol and vacuum dried. Chemical analyses of one gram aliquots showed 24 p.p.m. bromide and a water content of 0.41%. The purified bromate, which was stored over $CaCl_2$, appeared to be stable for at least six months as shown by periodic analyses.

The analysis for total bromine (bromide + bromine + hypobromite) produced in the $KBrO_3$ by radiation decomposition was conducted first using a colorimetric procedure based on the bromination of phenol red in alkaline solution,[5] and subsequently by a micro-potentiometric titration with 0.01 *N* $AgNO_3$. This latter procedure[6] involved dissolving a few hundred milligrams of the irradiated salt in water containing 150 λ of a 2% sodium arsenite solution which served to reduce all the forms of bromine present in the crystal except bromate to bromide. The potentiometric method is believed reliable down to a total bromine content of about 20 p.p.m. A blank determination was always performed at the same time.

Radioactivity measurements were made with a calibrated 4 π geometry ionization chamber of 20-liters volume filled with 40 atmospheres of argon.[7] The ion currents were amplified by means of a dynamic condenser electrometer whose output was fed into a continuous recording Brown potentiometer which indicated the instantaneous value of the activity as a function of time. The chamber was calibrated to correct for non-linearity in scale response owing to ion-recombination, for resistance ratios between scales, and for the dependence of the scale reading on the position of the sample in the measuring thimble. The estimation of absolute disintegration rates for radionuclides whose decay schemes were known was made possible by a careful measurement of the detection efficiency of the chamber as a function of gamma ray energies between 0.177 and 2.07 Mev. The decay scheme of Deutsch and Siegbahn[8] for radio-Br^{82} was used in the conversion of the observed ionization chamber readings to rutherfords (10^6 *d/s*) in the specific activity calculations given below. Because of its great stability and wide range for activity detection, this ionization chamber electrometer arrangement was well suited for an accurate half-life measurement of Br^{82} which was found to be 35.87 ±

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(3) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462 (1934).

(4) R. R. Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

(5) Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1936.

(6) P. F. Thomasson, private communication.

(7) C. J. Borkowski, *Anal. Chem.*, **21**, 348 (1949).

(8) M. Deutsch, *Phys. Rev.*, **61**, 672 (1942); K. Siegbahn, A. Hedgran and M. Deutsch, *ibid.*, **76**, 1263 (1949).

0.05 hours.[9] A measurement of the slow neutron capture isotopic cross-section for stable Br^{81} gave 2.8 barns.

Radioactive bromine was separated as follows: A few hundred milligrams of irradiated $KBrO_3$ were dissolved in water and the solution made up to 25 ml. Aliquots were pipetted into actinic glass separatory funnels, bromine water was added and the mixture extracted with an equal volume of carbon tetrachloride.[10] Two extractions of the aqueous phase were conducted to insure a quantitative separation. In some experiments the bromine activity was re-extracted back into water with bisulfite in order that no foreign activities be measured. It was observed, however, that the recovery from the organic phase was not quantitative since even after repeated washing 2–3% of the activity remained in the carbon tetrachloride, possibly because of a bromination reaction. Since accurate determinations of the decay rates of the organic layers gave a 35.9 h half-life, the re-extraction step was not continued. Activity measurements were also performed on the extracted aqueous $KBrO_3$ solutions. The observed activities were corrected to a common zero taken as the end of the bombardment. At the end of the irradiations the $KBrO_3$ samples contained appreciable amounts of the shorter lived 4.4 h and 17.5 m Br^{80} as well as 12.8 h K^{42} activities. Consequently, the separation and measurement of the 35.9 h Br^{82} activity was performed after a sufficient time elapsed (usually one week) to allow for the decay of these shorter periods. The ratio of the bromine activity in the organic layer to the total bromine activity initially in the irradiated potassium bromate serves to define the recovery factor, ϕ_t. Repeated determinations showed ϕ_t to be reproducible usually to better than 2%.

The neutron irradiations were carried out on one-gram samples sealed in air in quartz ampoules which were transferred to the pneumatic tube terminal near the center of the Oak Ridge pile. These bombardments were monitored using weighed cobalt wires whose induced activities subsequently were measured in the ion chamber described. The thermal neutron flux (*i.e.*, full source intensity) at this position so determined was $nv = 6.7 \times 10^{11}$ neutrons/cm.²/sec.

A preliminary investigation was made to find out if an appreciable thermal decomposition of potassium bromate could occur during the irradiation by estimating the temperature at the point where the samples were bombarded to be *ca.* 80°, and then heating weighed aliquots at this temperature in an air oven. Chemical analyses showed the thermal decomposition was negligible.

Several experimental studies were made to determine if a significant thermal exchange tending to lower the recovery of radiobromine occurred either: (1) in the crystalline bromate during irradiation or upon standing at room temperature afterwards; (2) during the dissolving of the irradiated crystals because of a surface-catalyzed reaction; or, (3) because of a reaction in homogeneous aqueous solution between the various oxidation states accessible to the recoiled Br^{82} and bromate. Repeated determinations of the recovery from the irradiated salt allowed to stand up to 150 hours at room temperature showed no changes in ϕ_t. At 80°, however, a slight decrease was observed which amounted to 5% after 64 hours of heating after irradiation.

The occurrence of a possible surface reaction seemed to be excluded by the following observations: (a) The recovery was measured in an experiment in which crystals previously irradiated for 24 hours were dissolved directly in bromine water. A value (0.70) within the experimental error of that obtained (0.69) upon dissolving in pure water was observed. (b) Irradiated bromate was dissolved in a $KBrO_3$ solution, bromine water was added after a brief period and the mixture extracted. A value of 0.69 was observed. (c) No change in ϕ_t was found when the irradiated bromate was dissolved in an aqueous solution made from strongly irradiated $KBrO_3$ whose radioactivity had disappeared by decay. (d) An aqueous solution containing small amounts of tagged bromate (*i.e.*, KBr^*O_3) was prepared in which, in separate experiments, pure and "dead" irradiated $KBrO_3$, respectively, were dissolved. Subsequently bromine water was added and an extraction was made. No radiobromine was detected in the organic phase.

The preliminary observation[11] that no exchange occurs between Br^-, Br_2 and BrO_3^- in neutral aqueous solutions was carefully checked under the conditions of the foregoing radiochemical separation procedure, since the slight hydrolysis of the bromine water added lowered the *p*H to about 4. Radiobromine as bromide + bromine was mixed with inactive potassium bromate in the same relative proportion as in irradiated salt. Aliquots from this mixture were dissolved in water, allowed to stand for periods up to two hours and then carried through the separation procedure. In every case all the 35.9 h Br^{82} was extracted into carbon tetrachloride. A study of the exchange over a wide *p*H range confirmed its existence in solutions more acid than 10^{-3} *M*. It was concluded from these and other experiments which will not be described that no exchange occurs in the activity separation procedure employed, and that the extraction of separable radiobromine was quantitative.

Experimental Results and Discussion

Quantitative data on the amounts of inactive bromide formed in the radiation decomposition of $KBrO_3$ and on the recovery and specific activity of 35.9 h Br^{82} also formed in the neutron irradiations conducted in this study are presented in Tables I and II. An inspection of the second column of Table I shows that the decomposition increased

Table I

Specific Activity and Enrichment of 35.9 h Br^{82} Produced by a Szilard–Chalmers Reaction with Solid $KBrO_3$ in the Oak Ridge Pile (Irradiations at $nv = 6.7 \times 10^{11}$ Neutrons/Cm.²/Sec.)

Irradiation time (hours)	Decomposition[a] (Av. p.p.m. bromide)		Recovery factor[b] (ϕ_a)	*St* Measured specific activity (rd./mg.)	Ratio of total Br_2 atoms by decompn. to radio-Br^{82} atoms $\times 10^{-4}$	Enrichment factor (*E*)
0.25	17	(1)	0.80	746	5.4	22000
.50	31 ± 2	(3)	.77	818 ± 20	4.9	11900
.75	45	(1)	.76	824	4.9	8100
1.00	71 ± 7	(3)	.75	677 ± 68	6.0	5000
1.33	142	(1)	(.74)	500	8.1	2600
2.00	197 ± 20	(4)	.73	500 ± 40	7.5	1780
3.00	293	(1)	.72	472	8.6	1180
4.00	403 ± 32	(3)	.73	459 ± 40	8.8	870
6.00	528 ± 67	(3)	.72	508 ± 67	7.9	650
8.00	730 ± 50	(2)	(.72)	501 ± 30	8.1	490
10.0	863 ± 40	(2)	.72	500 ± 23	8.1	400
12.0	1140 ± 10	(2)	(.71)	439 ± 5	9.0	310
16.0	1563 ± 100	(2)	.69	400 ± 30	10.1	210
22.0	2198 ± 56	(2)	.69	371 }	10.9	
24.0	2267	(1)	.69	385 } 378 ± 10	10.5	148
46.0	4400	(1)	.70	319 }	12.7	
48.0	4911	(1)	(.69)	286 } 300 ± 20	14.2	71
64.0	6800	(1)	.67	238	17.0	47

[a] Number of independent determinations in parentheses.
[b] Value in parentheses interpolated from a smooth curve.

Table II

Specific Activity of 35.9 h Br^{82} Produced in Solid $KBrO_3$ by Recoil Following Slow Neutron Capture, and the Variation of Its Enrichment with the Source Intensity (Two-hour Irradiations)

Relative source intensity	Decomposition (Av. p.p.m. bromide)	Recovery factor	Measured specific activity (rd./mg.)	Enrichment factor (*E*)
0.20	49	0.73	425	7760
.40	89	.73	516	4310
.60	130	.72	511	2860
.80	170	.73	547	2220
1.00	221	.72	530	1700

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(9) J. W. Cobble and R. W. Atteberry, *Phys. Rev.*, **80**, 917 (1950).

(10) The addition of carrier bromine is not necessary to extract the radio-bromine; however, the procedure is shortened and the radioactivity can be concentrated into a few cc. if small amounts are used. Further, the presence of the carrier serves to effect the exchange of all the radio-bromine into an extractable form (except that in BrO_3^-).

(11) W. F. Libby, This Journal, **62**, 1930 (1940).

linearly with the time of irradiation. Similarly, the second column of Table II shows the direct proportionality of the decomposition to the source intensity. These findings confirm the hitherto assumed decomposition equation for the rate of formation of *inactive atoms*, N_t

$$dN_t/dt = Ik_T(N_0 - N_t) \cong I\,k_T N_0 \qquad (1a)$$
$$N_t = N_0\,[1\text{-exp}\,(-I\,k_T t)] \cong I\,k_T N_0 t \qquad (1b)$$

where $(N_0 - N_t)$ is the number of undecomposed molecules containing one atom of activating element per molecule; I, the neutron source intensity; and, k_T, the *total* radiation decomposition coefficient, taken as a measure of the stability of the compound to the total radiations emitted by the neutron source. This coefficient will be independent of the source intensity and irradiation time; it will depend, however, upon the nature of the compound and upon the character of the neutron source. A least squares treatment of the decomposition data (Table I) down to one hour gave a value of 97 p.p.m./hr. for k_T when the source intensity, measured by the slow neutron flux, was 6.7×10^{11} neutrons/cm.²/sec. Since the total decomposition even after 64 hours was only 0.68% the approximation indicated in Equations 1 will be fairly good. The linear time dependence of the decomposition suggests that probably a radiation induced back reaction was absent in this instance. However, much longer irradiations would be needed to establish this point.

The rate of formation of *active atoms*, N_t^*, is given by

$$dN_t^*/dt = I\sigma N_0\theta - \lambda N_t^* \qquad (2)$$

where σ is the isotopic activation cross-section; N_0, the total number of atoms of element being activated; θ, the relative abundance of the target isotope; and λ, the decay constant. The rate of formation of *chemically separable* radiobromine atoms N_s^* does not follow Equation (2), however. Further, there was a clear indication that some sort of radiation back-reaction involving them did occur, for (Column 3, Table I) the separable activity was not constant but diminished with increasing time.

Several equations, including one assuming that the radiation induced back-reaction of recoiled Br^{82} was first order, were derived and tested with the recovery data (Table I) after correcting for the small loss owing to thermal exchange mentioned earlier. Although all of these equations predicted a constant recovery after long times, none of them could be made to fit the data over the whole time interval. The observed approach of ϕ_t to an apparent limiting value was much more rapid than could be accounted for by a first order back-reaction. These theoretical considerations did, however, indicate that the apparent independence of ϕ_t on source intensity found in the two hour irradiations (Column 3, Table II) was not real. The relative contribution of the back-reaction after so brief an irradiation was smaller than the experimental errors in the recovery determinations. A demonstrable dependence of ϕ_t on source strength may be expected for a 100-hour bombardment.

Since no simple equation based on elementary considerations could be found for the variation of N_s^*, the semi-empirical relation

$$N_s^* = \phi_t N_t^* = \frac{\phi_t I\sigma N_0\theta}{\lambda}\,(1 - e^{-\lambda t}) \qquad (3)$$

was employed together with Equation (1b) to obtain an expression for the specific activity, S_t, of the separated atoms

$$S_t \equiv \frac{\lambda N_s^*}{N_t} = \frac{\phi_t\sigma\theta}{k_T\,t}(1 - e^{-\lambda t}) \qquad (4a)$$

and for the limiting specific activity at zero time, S_0

$$S_0 = \phi_0\sigma\theta\lambda/k_T \qquad (4b)$$

A value of 615 rd./mg. Br for S_0 was estimated using the extrapolated value of $\phi_0 = 0.91$ and $\sigma = 2.78 \times 10^{-24}$ cm.²/atom Br^{81}, $\theta = 0.494$, $\lambda = 1.93 \times 10^{-2}$ hr.⁻¹ and $k_T = 97$ p.p.m./hr. A comparison between the specific activities computed from Equation (4a) and those observed is afforded by Fig. 1. Excepting for irradiations shorter than one hour in duration, the agreement is within the experimental errors involved. According to Equation (4a) the specific activity should be independent of the intensity of the slow neutron source. This was confirmed by irradiations in which the exposure time was kept constant at two hours (Table II).

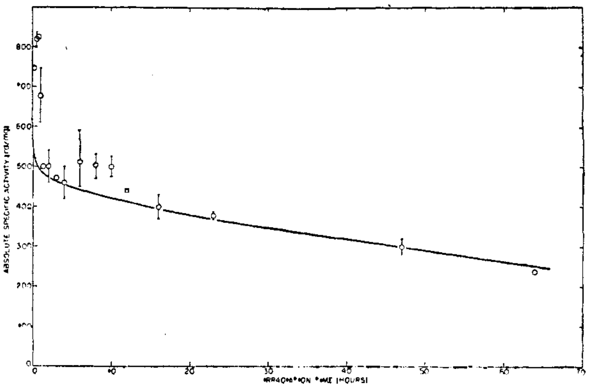

Fig. 1.—Variation of the specific activity of separable 35.9 h Br^{82} produced by neutron irradiation of crystalline $KBrO_3$ with time. Solid line according to Eq. 4a using observed values of ϕ_t in Table I.

It is also useful in discussing recoil reactions to define an enrichment factor, E, by the ratio of the Szilard–Chalmers specific activity to the specific activity attainable with a non-enriching radioisotope producing method

$$E \equiv \left(\frac{\lambda N_s^*}{N_t}\right) \bigg/ \left(\frac{\lambda N_t^*}{N_0}\right) = \phi_t \Big/ (1 - e^{-Ik_T t}) \cong \phi_t/Ik_T t \qquad (5)$$

Equation (5) shows that for a given compound the enrichment will diminish with increasing time and neutron source strength. These predictions are borne out by the entries in the last columns of Tables I and II, respectively, as well as by Fig. 2.

Insofar as Equations (4) and (5), which have seemed to describe the Szilard–Chalmers process in solid $KBrO_3$, may be applied to other compounds, certain generalizations may be made. Evidently, (Fig. 2) quite high enrichments can be obtained

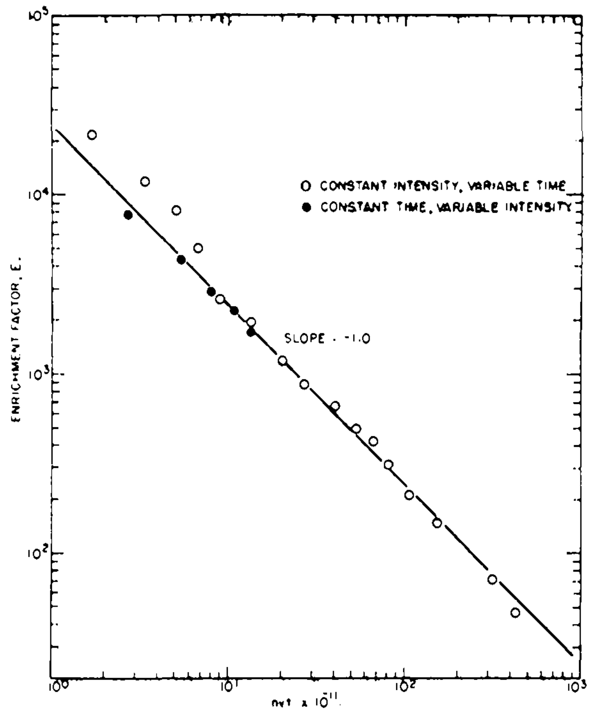

Fig. 2.—Variation of the enrichment of 35.9 h Br^{82} separable from neutron irradiated crystalline $KBrO_3$ with exposure (time expressed as hours).

either by short irradiations, or by the employment of low intensity sources. If an enrichment of 5000 for Br^{82} is found after a one-hour exposure in a slow neutron flux of 6.7×10^{11} n/cm.^{2}/sec., then a value of 5×10^5 might be expected for an intensity of 6.7×10^9 (typical of cyclotron sources) and of 5×10^8 for an intensity of 6.7×10^6 n/cm.^{2}/sec. which is of the order of magnitude of fluxes sustained by Ra + Be neutron sources. Interestingly, although very few data can be found in the literature, the values of 10^7 for the enrichment of P^{32} produced by a recoil reaction with triphenyl phosphate[12] and of 10^8 for I^{128} from ethyl iodide[13] are of this latter order of magnitude. A somewhat smaller enrichment (10^5) than would be expected has been reported in the preparation of 2.59 h Mn^{56} from $KMnO_4$.[14] Despite the high enrichment with weak neutron sources it is emphasized that the specific activity of the separated radioisotope will be independent of the strength of the source.

From the foregoing considerations, the advantage of the Szilard–Chalmers effect should disappear as progressively more intense slow neutron sources become available. However, at present, a quite worthwhile 90-fold enrichment of 35.9 h Br^{82} may be achieved by irradiating pure crystalline $KBrO_3$ for one half-life in a flux of 6.7×10^{11} n./cm.^{2}/sec.

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(12) O. Erbacher and K. Phillip, *Z. physik. Chem.*, **179A**, 263 (1937).

(13) O. Erbacher and M. Beck, *Z. anorg. Chem.*, **252**, 357 (1944).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Absorption Spectra of Some Diaryl Ketones, Hydrazones and Azines

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The comparison of the spectra of a number of diaryl ketones, their hydrazones and azines permits the classification of the observed absorption peaks into the following categories: (1) the peaks which result from the conjugation of the aryl group with the double bond of the carbonyl group, and which are also found in the hydrazones and azines of the ketones. (2) the peaks which result from the resonance which traverses the whole length of the azine molecule; (3) the peaks which correspond to the resonance of the aryl portions of the molecules, or which are traceable to the contributions by individual structural features (*i.e.*, the phenylmercapto- or the phenylsulfonyl groups).

In order that a better understanding may be obtained of the ultraviolet absorption spectra of a series of diaryl ketazines there were also investigated the spectra of the corresponding ketones and hydrazones. Of the diaryl ketazines only that derived from benzophenone seems to have been studied spectrophotometrically.[2] The substituted benzophenone azines are closely related to the recently described azines of substituted acetophenones.[3]

Experimental Results

The hydrazones and azines employed in this study were prepared by the methods developed in this Laboratory.[4] The physical properties and analytical data for the new compounds are listed in Table I. The absorption spectra were determined by means of a Beckman DU spectrophotometer employing solutions in 95% ethanol. The absorption curves are reproduced in Figs. 1–4, and the spectral data are summarized in Table II.

Discussion

The comparison of the spectra of the ketones and the corresponding hydrazones and azines permits the classification of the observed maxima into several groups related to each other from the viewpoint of the probable electronic transitions responsible for their appearance.

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(1) A portion of this material is taken from the M.S. thesis submitted by C. M. to the Faculty of the Graduate School of Duquesne University in June, 1950. Present address of C. M., The Massachusetts Institute of Technology.

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(3) H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4981 (1950).

(4) H. H. Szmant and C. McGinnis, *ibid.*, **72**, 2890 (1950).