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Nuclear Fission and the Transuranium Elements

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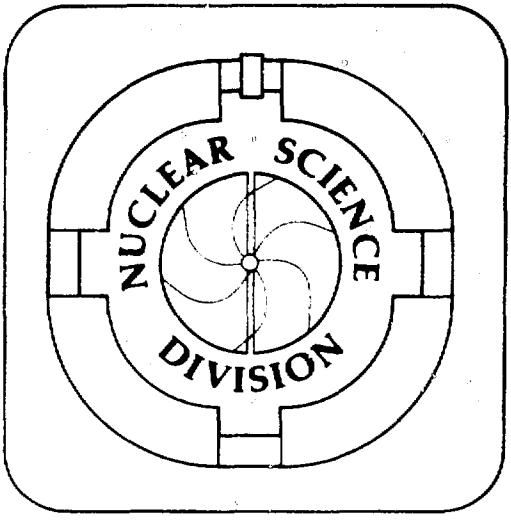

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NUCLEAR FISSION AND THE TRANSURANIUM ELEMENTS

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Presented at the conference "Fifty Years with Nuclear Fission"
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We are near the 50th anniversary of the synthesis and identification (i.e., the "discovery) of the first transuranium elements, neptunium and plutonium. The intervening years have seen the addition of 15 more transuranium elements with the result that this group now consists of 17 known elements, extending from neptunium (atomic number 93) through the unnamed element with atomic number 109.

Thus the addition of the transuranium elements to mankind's natural heritage of elements has led to an expansion of about 15% in the fundamental building blocks of nature. Investigation of these manmade elements beyond uranium has led to a tremendous expansion of our knowledge of atomic and nuclear structure. Each of these elements has a number of known isotopes, all radioactive, the overall total being about 200. Predictions indicate an additional 500 should have half-lives sufficiently long to allow identification (greater than 10^{-6} seconds). Synthetic in origin, they are produced in a variety of transmutation reactions by neutrons or charged particles, including heavy ions. (Neptunium and plutonium are, in addition, present in nature in very small concentrations.) There is a total of 30 isotopes with half-lives long enough to be available in macroscopic (weighable) quantities.

Many of the transuranium elements are produced and isolated in large quantities through the use of neutrons furnished by nuclear fission reactions: plutonium (atomic number 94) in ton quantities; neptunium (93), americium (95), and curium (96) in kilogram quantities; berkelium (97) in 100

milligram quantities; californium (98) in gram quantities; and einsteinium (99) in milligram quantities. Transuranium isotopes have found many practical applications--as nuclear fuel for the large-scale generation of electricity, as compact, long-lived power sources for use in space exploration, as means for diagnosis and treatment in the medical area, and as tools in numerous industrial processes.

Of particular interest is the unusual chemistry and impact of these heaviest elements on the periodic table. This account will feature these aspects.

Prefission and Fission

Our initiation into the realm of the transuranium elements came in the spring of 1940, when Edwin M. McMillan and Philip H. Abelson proved that the radioactive product of their fission experiments was actually a new element--the first identifiable member of the transuranium family. In the 50 years following that discovery, teams of scientists have tried to increase our knowledge of nature by expanding the periodic table of the elements. Looking at the events since late 1938 when fission was discovered not only illustrates how much more has been learned, it also helps dispel the idea that good scientists--even top scientists working together--don't miss the obvious answer on occasions.

To really appreciate the number of false starts--the erroneous paths we took toward the discovery of the new elements--we need to go back to the beginning. And the beginning was in 1869, when Dmitri Ivanovich Mendeleev, a Russian chemist, proposed an arrangement of chemical elements that not only took into account similarities among known elements but also provided the framework for predicting then-unknown entries.

Using the periodic table (Fig. 1) of the 1930's, Enrico Fermi, the great Italian physicist, thought that if he could operate on uranium some way--transmute it--why couldn't he produce element 93, and maybe element 94? According to this periodic table, elements 93 and 94 would have chemical properties similar to those of rhenium and osmium, respectively. Fermi and coworkers (Emilio Segrè, Edoardo Amaldi, Franco Rasetti and O. D'Agostino) planned to start with the heaviest element, actually by bombarding it with neutrons, and then hope that after it captured a neutron it would emit an electron (that is the same thing as increasing its charge by one), losing a negative charge, and that way go up to element 93. So they bombarded uranium with neutrons, forming a number of radioactive isotopes. It was of course expected that these isotopes would be radioactive because they do not exist on Earth; they had decayed away.

Fermi and his co-workers in 1934 thought that they chemically proved that one of the isotopes, with a half-life of 13 minutes, had chemical properties like those expected for element 93, i.e., chemical properties like those of rhenium.

For several years the so-called transuranium elements were the subject of much experimental work and discussion. Experiments in Germany by Otto Hahn, Lise Meitner, and Fritz Strassmann seemed to confirm Fermi's view. A series of papers published between 1935 and 1938 reported not only eka-rhenium--that which resembles rhenium--but also eka-osmium, eka-iridium and eka-platinum (atomic numbers 93, 94, 95, and 96).

There was, however, one person who didn't believe that these discoveries were transuranium elements. In 1934, Ida Noddack wrote a paper asking if these observations could not be due to isotopes in the middle of the periodic table. Fermi had not proved that the decay products were transuranium

elements. Even then, however, we didn't see the light. This paper was in the literature from the beginning and was ignored.

Early in 1939, Hahn and Strassmann described experiments that confirmed that they had observed radioactive barium and lanthanum isotopes as a result of the bombardment of uranium with neutrons. Hahn and Strassmann were absolutely nonplussed by their results, and the tone of that 1939 paper was more or less along the lines of: "You're not going to believe this, but this is what we found -actually, when you bombard uranium with neutrons, you get barium." Subsequent work showed that the other radioactivities previously ascribed to transuranium elements are actually also due to uranium fission products.

I remember when this news came to Berkeley. It was reported at what was called the Journal Club in the Physics Department, a meeting that I attended every Monday night. Somebody got up and said, "You know, all of these transuranium elements that Hahn and Strassmann have been finding were due to the splitting of uranium in half..." Before he had finished the sentence, I said to myself, "My God, how stupid we have been! Obviously, that should be the explanation."

Neptunium and Plutonium

With poetic justice the actual discovery of the first transuranium element resulted from experiments aimed at understanding the fission process. During an investigation of the fission process, McMillan discovered a radioactive isotope of 2-day half-life. Working at the University of California at Berkeley in the spring of 1939, he was trying to measure the energies of the two main recoiling fragments from the neutron-induced fission of uranium. He found that the isotope with the 2-day half-life did not recoil sufficiently to escape.

McMillan suspected this observation could be due to the fact that the isotope was not a fission product but rather a new entity--element 93. However, he was not able to prove this until Phil Abelson joined him in Berkeley in the spring of 1940. They found that the isotope could be chemically separated from all the other elements in the periodic table. Its chemistry was entirely different from that which had been predicted by Hahn, Strassmann, and the rest of us. It was chemically like uranium and not at all like rhenium . Element 93 was given the name neptunium (Np) because it is beyond uranium, just as the planet Neptune is beyond Uranus. Soon after this, a team consisting of McMillan, J. W. Kennedy, A. C. Wahl, and myself bombarded uranium with deuterons (nuclei of hydrogen atoms of mass number 2) and found an isotope of neptunium, which upon decay led to an alpha-particle-emitting isotope, which although chemically similar to neptunium and uranium was different. After chemical separation of this alpha-particle-emitting material, we were able to show that we had in fact prepared a new element. The name plutonium (symbol Pu), after the planet Pluto, was suggested for element 94 in a secret report written on March 21, 1942, but not actually published until after the war.

At this time we thought that the transuranium elements had the same kind of relationship as the rare earths --a new group of rare earths -and there should be 14 of them, with uranium as the prototype. This we would call the uranide series, just like the lanthanide series. It was on this basis that we predicted that element 95 and element 96 would be like plutonium, neptunium, and uranium--a little different, but more or less the same. Wrong again! We were just slow learners; we had to proceed by making mistakes. When we tried by transmutation reactions to produce elements 95 and 96 by this method and chemically identify them, we could not do it.

The Revised Periodic Table

In 1944, I got the idea that maybe these elements were misplaced in the periodic table. Perhaps the new heavy rare earth series should start back at thorium (Fig. 2) with actinium as the prototype--thus dubbing the collection the actinide series. With such an arrangement the position of elements 95 and 96 would suggest that they be chemically similar to europium and gadolinium. When we tried this idea, we found that it was right. We identified elements 95 and 96. A year later, I published the rearrangement of the periodic table in Chemical and Engineering News. I remember at the time that I showed this table to a number of my friends and said that I contemplated publishing it in Chemical and Engineering News, they said, "Don't do it, you'll ruin your scientific reputation." I had a great advantage--I didn't have any scientific reputation at that time--so I went ahead and published it.

This concept had great predictive value, and its success led to the discovery of the remainder of the actinide elements and its acceptance by the scientific community. The modern periodic table contains not only a full lanthanide series, but a full actinide series and transactinide elements as well.

The discovery of elements 95 and 96 was announced for the first time on "The Quiz Kids," a radio program. I was a guest on the program in Chicago on November 11, 1945, Armistice Day, and the moderator turned the format around so that the Quiz Kids asked me questions for the last 15 minutes of the show (Fig. 3). One of the kids, Richard Williams, asked me, "One other thing now, have there been any other new elements discovered like plutonium and neptunium?" Our work had just been declassified so that I could present a paper the next Friday afternoon at an American Chemical Society symposium at Northwestern University, so I replied, "Oh yes, Dick. Recently, there have

been two new elements discovered, elements with atomic number 95 and 96 out at the Metallurgical Laboratory here in Chicago." This was the only time in the history of the world that the announcement of the discovery of chemical elements was sponsored by Alka Seltzer.

So, now we have the actinide series terminating at element 103. The elements beyond element 103 are referred to as transactinide elements. The first three of the transactinide elements --rutherfordium (element 104), hahnium (105), and the unnamed element 106 --have been synthesized and identified by Albert Ghiorso and co-workers at Berkeley. Competing claims for the discovery of these three elements have been made by G. N. Flerov and co-workers of the Dubna Laboratory in the Soviet Union; for this reason no name has been suggested for element 106.

Element 107, 108, 109 -and more?

I shall describe the research on the heaviest transuranium elements in some detail. Due to competing claims for the discovery of these elements, no names have been suggested.

During the 1980s, investigators working at the Gesellschaft für Schwerionenforschung (GSI) at Darmstadt, Federal Republic of Germany, synthesized and identified (i.e., discovered) isotopes of the elements with atomic numbers 107, 108, and 109, produced by the "cold fusion" reaction bombardments of target nuclides in the region of closed nucleon shells at lead and bismuth with heavy ions furnished by the UNILAC accelerator. The potential efficacy of such a reaction was first suggested in 1974 by Y. T. Oganessian and demonstrated by Oganessian and coworkers working at the Joint Institute for Nuclear Research at Dubna in the Soviet Union. The expectations were to observe product nuclides with odd numbers of nucleons (odd-even, odd-odd, or even-odd) because these have substantially longer half-lives for decay by alpha-emission or spontaneous fission than do even-even nuclides.

G. Münzenberg et al. in 1981, working at GSI, clearly identified the nuclide $^{262}107$ produced in the "cold fusion" reaction $^{209}_{83}Bi + ^{54}_{24}Cr \dashrightarrow {}^{262}107 + {}^{1}_{0}n$. The recoiling product nuclei from the nuclear reaction were passed through a velocity separator called SHIP (Separator for Heavy Ion Reaction Products) which guaranteed that they had the characteristic velocity of the product of complete fusion of projectile and target nuclei. The products were implanted into position sensitive surface barrier detectors. The mass number of the velocity-separated product nucleus was determined approximately by measuring its time of flight and its atomic number and mass number were determined by observing the time-correlated alpha-decay to the previously known daughter, $^{258}_{105}Ha$, granddaughter, $^{254}_{103}Lr$, etc. (the method of genetic relationship). A total of about five alpha-decays of $^{262}107$ were observed with an energy of 10.4 MeV and half-life of approximately 5 milliseconds (ms). The cross section for producing these nuclei was 2×10^{-34} cm^2, i.e., 0.2 nanobarns (nb), approximately 1/5,000,000 of the production cross section observed in the first one-atom-at-a-time experiment in the discovery of mendelevium (atomic number 101). In other experiments Münzenberg et al., with the same target-projectile combination and by the method of genetic relationship, identified a few atoms of the isotope $^{261}107$ with a 6 ms half-life and an alpha-energy of about 10.1 MeV and a few atoms of an isomer of $^{262}107$ with a 56 ms half-life and an alpha-energy of about 9.8 MeV. By 1988, a total of 38 atoms of Element 107 had been observed, 14 atoms of $^{262m}107$ with a half-life of 8 ms and 10.3 MeV alpha-particles, 15 atoms of 100 ms $^{262}107$ (9.9 MeV alpha-particles), and 9 atoms of 9 ms $^{261}107$ (10.1 MeV alpha-particles). Also using the same target-projectile combination Oganessian et al. identified ^{246}Cf, which they claimed to be a decay descendant of $^{262}107$.

Oganessian et al. in 1976, working in the Joint Institute for Nuclear Research at Dubna in the Soviet Union, had reported the production in a cyclotron of an isotope, which decayed by spontaneous fission (SF) with a half-life of approximately 2 ms, from the reaction of $^{209}_{83}$Bi with $^{54}_{24}$Cr, which they attributed to ^{261}107. However, the evidence is not sufficient to assign an atomic number.

Münzenberg et al. in 1984, identified three atoms of Element 108, in the form of the isotope ^{265}108, produced by the $^{208}_{82}$Pb ($^{58}_{26}$Fe, 1n) reaction, again by the method of genetic relationship. The nuclide decayed with a half-life of approximately 1.8 ms, emitting alpha-particles with an energy of 10.36 MeV. The cross section for production of these nuclei was 1/10 of that observed for the production of Element 107 (i.e., approximately 2 x 10^{-35} cm^2 or 20 picobarns). In a second experiment one atom of the isotope ^{264}108 (half-life approximately 80 microseconds) was produced by the ^{207}Pb (^{58}Fe, 1n) reaction and identified by the method of genetic relationship. It was notable that this heaviest known even-even nuclide decays by alpha-particle emission rather than by spontaneous fission and that it has so relatively long a half-life.

Also in 1984, Oganessian et al. reported the very indirect observation of the possible alpha-decay of ^{263}108, ^{264}108, and ^{265}108 produced in the reactions $^{209}_{83}$Bi ($^{55}_{25}$Mn, 1n), $^{207}_{82}$Pb ($^{58}_{26}$Fe, 1n), and $^{208}_{82}$Pb ($^{58}_{26}$Fe, 1n), respectively. None of the alpha-particle decays of the Element 108 isotopes were observed directly. Identification was surmised on the basis of observation of descendants from alpha decay--^{255}104 from ^{263}108, ^{256}104 from ^{264}108, and ^{253}Es from ^{265}108. However, such inferences cannot be accepted as proof of the discovery of an element because the observed activities could have been produced directly.

Münzenberg et al. in 1982, after eleven days (equivalent) of bombardment, observed one unusual time-correlated decay sequence that occurred for a reaction product that had been velocity-separated by SHIP from the $^{209}_{83}Bi + ^{58}_{26}Fe$ reaction. The product $^{266}109$, which decayed in 5 ms (half-life 3.5 ms) with the emission of an 11.1 MeV alpha-particle, was partially identified by the method of genetic relationship. Such a yield corresponds to a formation cross section of very approximately 10^{-35} cm^2, or 10 picobarns. In a second experiment, in 1988, two more time-correlated decay sequences similar to the first were found.

Oganessian et al. in 1984 used the ^{209}Bi (^{58}Fe, n) reaction to identify ^{266}Cf, which they inferred to be a decay descendent of $^{266}109$.

Oganessian et al. in 1987 reported the production in the reaction of $^{44}_{20}Ca$ with ^{232}Th, with a cross section of 8 picobarns, of a 9 ms spontaneous fission activity, which they assigned to an isotope of element 110 (possibly $^{272}110$). A similar activity was also produced, and so assigned, in the reaction of $^{40}_{18}Ar$ with $^{235,236}_{92}U$. The evidence is not sufficient to assign an atomic number. An attempt by a GSI team to observe this activity from the reaction of ^{40}Ar with ^{235}U, using SHIP, led to negative results. Additional exhaustive attempts by a GSI team to produce and identify element 110 by the reaction $^{208}_{82}Pb + ^{64}_{28}Ni$ ---> $^{271}110 + 1n$ have also led to disappointment. A. Ghiorso is attempting another approach through the reaction $^{209}_{83}Bi + ^{59}_{27}Co$ ---> $^{267}110 + 1n$, using a rebuilt version of SASSY (Small Angle Separating System), a gas-filled on-line recoil separator, to separate and identify the expected product.

The names and symbols of the known transuranium elements are summarized below:

Transuranium Elements

93	NEPTUNIUM	Np
94	PLUTONIUM	Pu
95	AMERICIUM	Am
96	CURIUM	Cm
97	BERKELIUM	Bk
98	CALIFORNIUM	Cf
99	EINSTEINIUM	Es
100	FERMIUM	Fm
101	MENDELEVIUM	Md
102	NOBELIUM	No
103	LAWRENCIUM	Lr
104	RUTHERFORDIUM	Rf
105	HAHNIUM	Ha
106	Unnamed	
107	Unnamed	
108	Unnamed	
109	Unnamed	

Future Prospects

Today we know of 17 transuranium elements, and we hold out hope for the production and identification of still further elements. As indicated, beyond 106, half-lives become short and yields become extremely small (with element 106, the yield is only a few atoms per day, at 109 the yield is much smaller--one atom per week); at this point, identifications are very hard to make. There are theoretical indications however that, if you think big, moving into a region where there might be another closed proton or closed neutron shell, the nucleus will become relatively more stable and longer lived and the yields will become larger.

Calculations based on modern theories of nuclear structure have shown that in instances where the proton number equals 114 or the neutron number equals 184 (these are known as closed nuclear shells or magic numbers), the ground states of nuclei should be stabilized against decay by spontaneous fission. Such stabilization, particularly if both numbers 114 and 184 could be reached, should lead to half-lives that are sufficiently long to allow detection, whereas in the absence of this stabilization, the half-lives would be too short to allow the nuclei to exist at all, due to decay by spontaneous fission.

The circumstance of such "superheavy elements" has been optimistically mapped as the "island of stability" and separated from the "peninsula" of known nuclei by a "sea of instability" (Fig. 4). To approach the island of stability, large numbers of neutrons, as well as protons, must be added using heavy ions to bombard heavy target nuclei.

It has not yet been possible to reach the island of stability for either or both of two possible reasons: either the reactions tried so far just do not produce superheavy elements (due to failure to produce products with as many as 184 neutrons), or the map of the island of stability is not correct. For example, one reaction tried in the Berkeley, GSI and Dubna laboratories, is fusion -fusing together two nuclei until they add up to the atomic number 114 or thereabouts. Unfortunately, the nuclei just don't seem to fuse when both components are too heavy. Most of the effort has been based on the reaction of ^{48}Ca with ^{248}Cm. Those that do fuse lead to such excited products that much more than 99% of the time they undergo fission leaving only an extremely small quantity to identify as a superheavy element. However, we are still hopeful that the reaction of ^{48}Ca with heavier target nuclei such as ^{254}Es might work; this has the potential to give a product with close to 184 neutrons.

Attempts to synthesize and identify superheavy elements through bombardments of a wide range of heavy nuclides with varieties of heavy ions have not yet been successful. Nevertheless, a great deal of effort has been expended to predict the chemical properties of the superheavies. If and when they are produced, we would like to have a procedure for their chemical identification. As always we are in danger of misinterpreting the periodic table while trying to make our predictions of chemical properties fit into the scheme.

The transactinide elements begin with element 104, the first element beyond lawrencium (number 103, the heaviest actinide element), and extend, in principle, indefinitely. Chemical properties can be predicted using the periodic table and by calculating electronic structures using modern atomic computer programs. Elements 104 to 112 should constitute the 6d transition series; elements 113 to 118 complete the 7p shell; elements 119 and 120 complete the 8s shell; and a new inner transition series of 32 rare-earth like elements (6f and 5g shells), the superactinides, is expected to begin following element 121, superactinium, and end at element 153. Elements 154 to 168 would involve the filling of the 7d and 8 p shells, with element 168 expected to be a nobel gas (actually a nobel liquid because its boiling point should be above room temperature). Relativistic effects suggest chemical properties for transactinide elements noticeably different then those of their lighter homologs. Our periodic table (Fig. 5) predicts that element 114 should be chemically like lead.

However, there appears to be no hope of synthesizing and identifying heavy elements beyond the island of stability around element 114 due to nuclear instability and lack of accessible nuclear reactions.

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Figures:

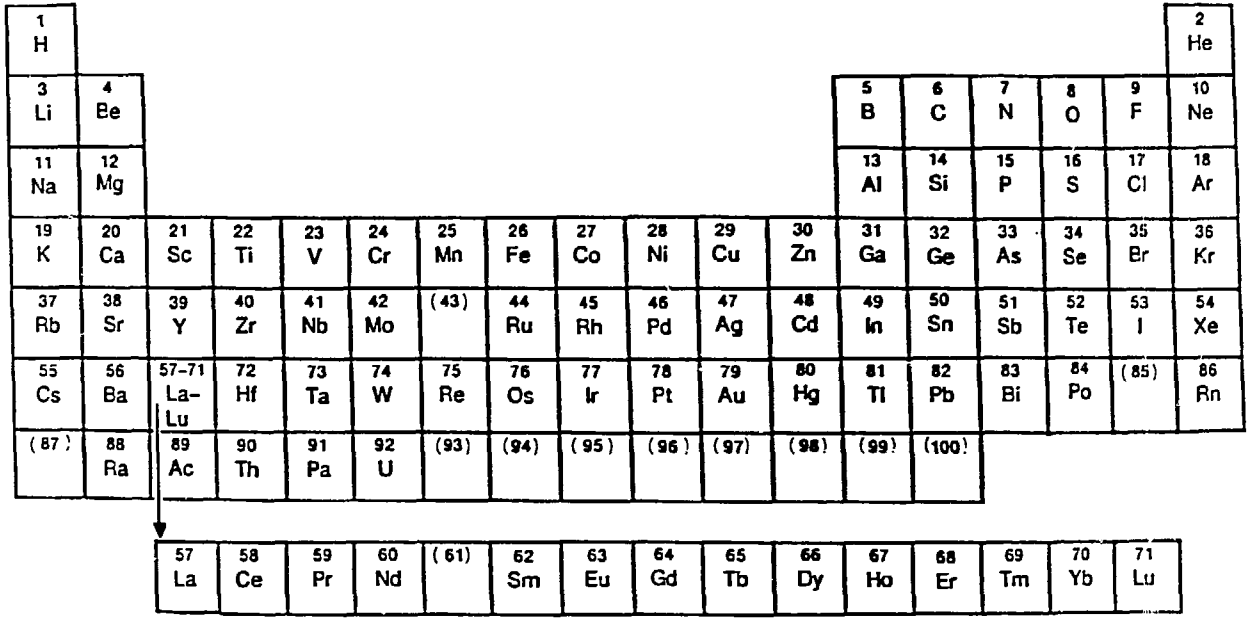
Fig. 1. Periodic Table of the 1930's. Atomic numbers of undiscovered elements are shown in parentheses. XBL 769-10601 (E1x)

Fig. 2. Periodic table published by the author in 1945, showing the heaviest elements as members of an actinide series. XBL 769-10603 (E 3)

Fig. 3. Quiz Kids Sheila Conlan and Robert Burke with the author when he informally announced discovery of elements 95 and 96 on a radio show in 1945. XBB 764-2297 (H61)

Fig. 4. This "map" of the peninsula of known elements and the island of stability represents the optimistic view of the discovery of superheavy elements. XBC 722-906 (G 10)

Fig. 5. Modern periodic table. Atomic numbers of undiscovered elements appear in parentheses. XBL 751-2036A (E 21C)



XBL 769-10601

Fig. 1

PERIODIC TABLE SHOWING HEAVY ELEMENTS AS MEMBERS OF AN ACTINIDE SERIES

Arrangement by Glenn T. Seaborg, 1945

1 H 1.008																1 H 1.008	2 He 4.003
3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.997	12 Mg 24.32	13 Al 26.97										13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3
55 Cs 132.91	56 Ba 137.36	57 LA 138.92	58-71 SEE LA SERIES	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85	86 Rn 222
87	88 Ra	89 AC	SEE AC SERIES	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96							

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99
ACTINIDE SERIES	89 Ac	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu	95	96							

XBL 769-10603

Fig. 2

SHEILA CONLAN BOB BURKE NOV 11 1945

To see if this complexion is complete, the following experiment was accomplished. The sample containing 1 molar equiv of benzaldehyde and 1 molar equiv of Yb-complex in CH_2Cl_2 was subjected to an IR study. A strong absorbance at 1660 cm^{-1} was found, which was assigned to the carbonyl group in the complex of PhCHO-27. The absence of a peak at 1720 cm^{-1} for free benzaldehyde shows that the complexion of benzaldehyde and 27 is complete. Similar shifts were also observed in other substituted benzaldehydes.

In order to get an assessment of the role of the electronic effect on this reaction, different substituted benzaldehydes were studied. Table 3.2 summarizes the results obtained (plots shown in Appendix A).

Table 3.2

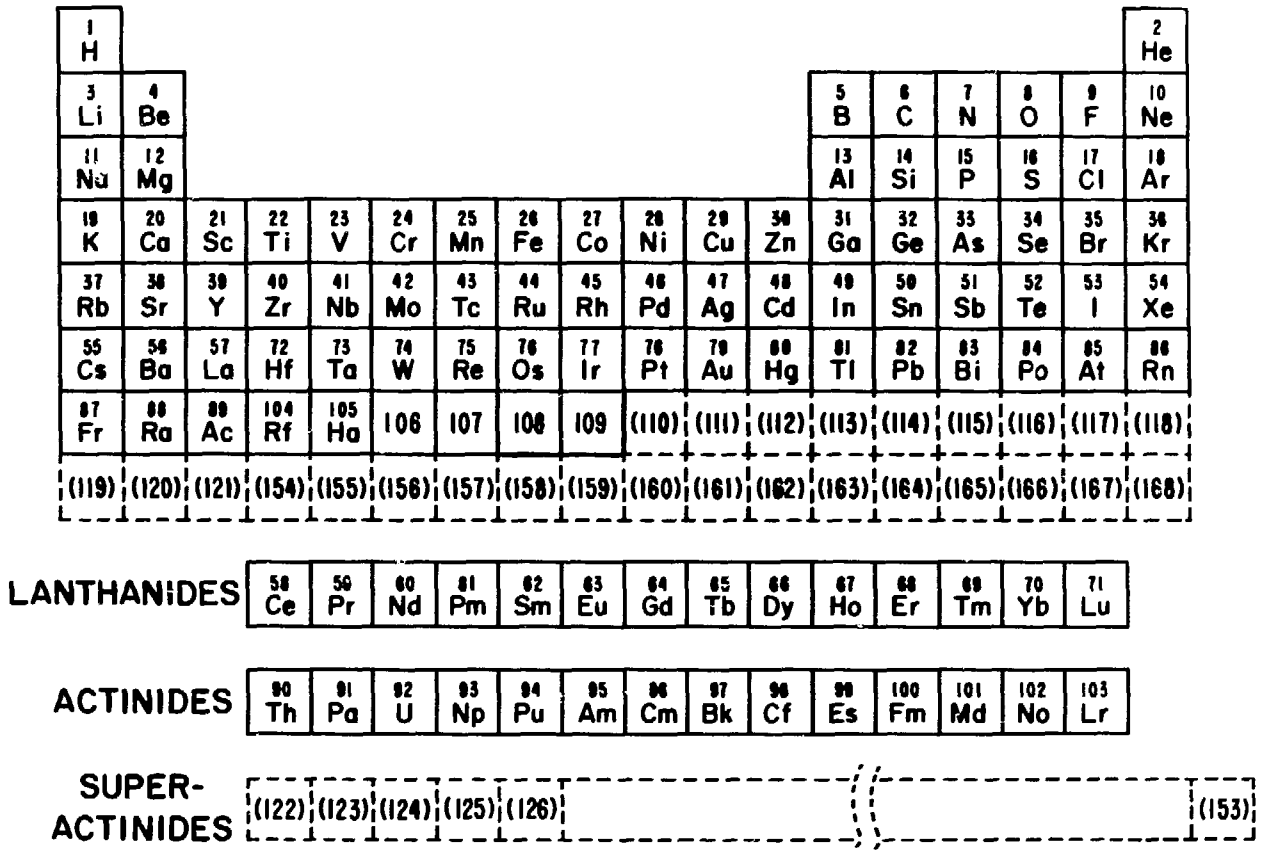
Rate Constants of XPhCHO

entry	X	28 (a)	27 (a)	XPhCHO(a)	k ($s^{-1}M^{-1}$)(b)
1	OCH_3	0.41	0.051	0.44	0.009
2	CH_3	0.40	0.045	0.48	0.12
3	Ph	0.40	0.046	0.41	0.14
4	F	0.42	0.023	0.47	0.16
5	H	0.41	0.046	0.44	0.17
6	Cl	0.38	0.043	0.42	0.20

a. the unit of concentration: M.

b. the probable error in the rate constants is 10%.

Examining the results, one can clearly see that electron withdrawing groups assist



XBL751-2036A

Fig. 5