breakdown or environmental modification that are the result of vasodilation and edema (*3, 8*).

The next phase of the syndrome, during which blood magnesium returns to normal level (*9*), has shown blanching of the skin and regranulation of the mast cells. However, the dermal mast-cell population was only about one-half of that of the controls at 28 days (Table 1); this indicates a slow rate of regeneration consistent with that of mast-cell damage by osmotic environmental changes (*3, 10*).

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Gibberellin Effects on Temperature and Photoperiodic Requirements for Flowering of Some Plants

Several physiologic responses in plants that heretofore have not been subject to chemical regulation may be controlled by gibberellin. Dwarfism, both genetic (*1*) and physiologic (*2*), may be overcome, and growth rates characteristic of normal varieties may be established. The cold requirement for flowering of the biennial *Hyoscyamus niger* has been replaced by treatment with gibberellin (*3*), and encouraging results with other biennials and annuals have now been reported (*4*). In this report (*5*), the induction of flowering with gibberellin in a large number of genera and species that were grown under environmental conditions not conducive to flowering is described.

All plants were grown from seed and maintained in pot cultures of soil in the greenhouse during the summer, fall, and winter of 1956–57. Treatment was initiated when the plants were at a stage, defined by leaf number or by stem or root size, at which exposure to cold or to long days would have resulted in a prompt flowering response. Gibberellin was applied, either as droplets of water solution on the apices of the plants or as an aqueous spray, to the foliage. Further details of the treating procedure, with a listing of the biennials and long-day annuals which have flowered with gibberellin under noninductive environments, are given in Table 1.

The biennials that were induced to flower with gibberellin were grown at temperatures slightly higher than the critical temperature for flower formation. That these temperatures (10° to 13°C) were noninductive was indicated by the absence of flowering in controls. The original finding (*3*) for *Hyoscyamus niger* was no exception. At temperatures of 18°C or above, extensive stem elongation was induced in cabbage, kale, beets, rutabagas, turnips, and celery, but flowering was not consistent. In contrast, gibberellin has caused stem elongation and flowering in carrots over a wide range of noninductive temperatures (13° to 25°C) and under short (9 to 11 hours), as well as long (14 to 16 hours), photoperiods.

With long-day annuals, flowering was induced under a noninductive environment of a short (9 to 11 hours) photoperiod and low (10° to 13°C) temperature. Under the same conditions, but in the absence of gibberellin, lettuce, endive, radish, spinach, dill, and mustard remained vegetative and acaulous.

Development of most gibberellin-treated biennials and annuals during flowering differed from that of the nontreated plants. On nontreated plants, bolting and flower initiation occurred simultaneously, while treated plants developed stems from 20 to 100 cm higher before flower buds could be identified.

Regardless of whether the effects of gibberellin on flower formation are direct or indirect, it has now been established that treatment with gibberellin, a naturally occurring plant product, has resulted in complete flowering responses. Often a single application is sufficient to induce flowering in a wide variety of economic crops grown under nonflowering conditions of temperature (the cold-requiring biennials) and photoperiod (long-day-requiring annuals).

Table 1. Cold-requiring biennials and long-day annuals in which flowering has been induced by gibberellin. (Plants grown under noninductive conditions.)

Biennials		Long-day annuals	
Plant	Treatment	Plant	Treatment
Brassica oleracea var. *capitata* (cabbage). Golden acre and Ferry's round dutch	100 µg weekly for 8 wk. First treatment at stem diameter of 1 cm and 7–9 leaves	*Anethum graveolens* (dill)	1 foliage spray of 100 ppm at 5–6 leaf stage
Brassica oleracea var. *acephala* (kale). Siberian and Dwarf blue curled	(As above for cabbage)	*Brassica pekinensis* (Chinese cabbage). Michihli	2 foliage sprays (3-wk interval) of 1000 ppm at 6–7 leaf stage
Brassica oleracea var. *acephala* (collards). Georgia and Louisiana sweet	100 µg weekly for 6 wk at 7–9 leaf stage and 1 cm stem diameter	*Brassica juncea* (mustard). Southern giant curled and tendergreen	100 µg weekly for 3 wk at 8–10 leaf stage
Brassica Napobrassica (rutabaga). Purple top	3 foliage sprays of 1000 ppm at 2-wk intervals at the 6–9 leaf stage	*Cichorium endivia* (endive). Full heart Batavian and green curled	100 µg weekly for 8 wk at 8–10 leaf stage
Brassica Rapa (turnip). Purple top	(As above for rutabaga)	*Lactuca sativa* (lettuce). Great Lakes	3 applications (4-wk interval) of 20 µg at 8–10 leaf stage
Daucus Carota var. *sativa* (carrot). Chantenay and Imperator	20–100 µg/plant when roots were 1 cm or larger in diameter	Bibb	2 applications (4-wk interval) of 20 µg at 8–10 leaf stage
Digitalis purpurea (foxglove)	100 µg/plant for 6 weeks at the 6–8 leaf stage or 1000 ppm foliage spray	Grand Rapids and Tendergreen	20 µg at 8–10 leaf stage
Bellis perennis (English daisy)	(As above for foxglove)	*Raphanus sativus* (radish). Crimson giant and Icicle	100 µg or foliage spray of 100 to 1000 ppm at 3–5 leaf stage
Matthiola incana (stock)	20–100 µg/plant at the 6–8 leaf stage or a foliage spray of 100 ppm	*Spinacia oleracea* (spinach). Prickly dark seeded	Foliage spray of 1000 ppm at 2–3 leaf stage, repeated after 4 wk
Viola tricolor (pansy)	(As above for stock)	*Petunia hybrida* (petunia)	Foliage spray of 10–100 ppm at 4–8 leaf stage

All cold-requiring biennials, when grown close to, but slightly higher than, the known inductive temperatures, have been induced to flower with gibberellin. Similarly, long-day plants, after treatment, have flowered under short photoperiods. Exceptions have not thus far been observed. Widespread usefulness of such findings will be realized in earlier flowering for seed production and in the commercial culture of many flowering annuals and biennials.

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Stepwise Reaction on Separate Catalytic Centers: Isomerization of Saturated Hydrocarbons

In heterogeneous catalysis, a chemical reaction may proceed by creation of an intermediate product on one type of catalytic center, creating a "true"—that is, existing independently in the desorbed state—intermediate at low concentration, which is then further reacted by another type of and physically distinct catalytic center. In a previous report (*1*), it was shown how physical transport processes lead to a general criterion for required physical proximity between the two types of catalytic materials, depending on the maximum attainable vapor pressure of the intermediate.

The experimental results reported in this article present evidence that this type of mechanism is operative in the catalytic isomerization of paraffin hydrocarbons by acidic solids (for example, aluminum silicates, or halogenated alumina) impregnated with small amounts of group VIII metals (*2*).

Reaction mechanisms proposed by Mills *et al.* (*3*) have included formation of intermediate olefinic species and surface migration between metal and acidic sites. Our results confirm the hypothesis of olefinic intermediates. They furthermore demonstrate (i), their existence as a true intermediate existing in the gas phase; (ii) the ability of metal and acidic sites to act as independent, physically distinct catalysts; and (iii) the role of ordinary gas-phase diffusion of intermediates between the consecutive reaction sites in supporting the over-all reaction rate, in quantitative agreement with the criterion developed in the previous report (*1*). Specifically, the four sets of experimental results reported here support a mechanism by which the isomerization of *n*-hexane over platinum-containing silica-alumina catalyst proceeds by the mechanism

$$n\text{-Hexane} \overset{\bullet}{\rightleftarrows} n\text{-hexene} \overset{\circ}{\rightleftarrows} \text{iso-hexenes} \overset{\bullet}{\rightleftarrows} \text{iso-hexanes}$$

where the hexenes are true, low-concentration gas-phase intermediates traveling by diffusion between independent Pt (●) and "acidic" catalyst sites (○).

At 373°C, thermodynamic data (*4*) show that the thermodynamically attainable relative concentration of hexenes in *n*-hexane at 1 atm hydrogen partial pressure is 0.6×10^{-2} if all *n*-hexene isomers are produced, or 3×10^{-2} if, in addition, all methyl-pentene isomers are formed. We have passed 11 g of *n*-hexane per hour over platinum catalyst at 373°C, at 5/1 hydrogen-hexane molar ratio and at atmospheric pressure and have found, by mass-spectrometric means, the concentration of C_6 olefins produced to be 2.7×10^{-2}. This magnitude is in agreement with that attainable at thermodynamic equilibrium.

High activity of acidic oxide catalysts such as aluminum silicates to catalyze the isomerization of olefins has been reported (*5*). Over silica-alumina catalyst (422 m^2/g surface area, 11 percent by weight Al_2O_3), we have obtained 43 percent conversion of *n*-hexene to isohexenes at a space rate of 2.6 cm^3 of liquid hexene per hour, per cubic centimeter of catalyst space and at a temperature as low as 300°C.

Table 1. Cooperative action of independent Pt and acidic particles (hexane feed-rate, 26 cm^3/hr).

Charge in reactor	*T* (°C)	Conversion to iso-hexane (% wt.)
i 4.7 g Pt/silica (10 cm^3)	373	0.9
ii 7.0 g Si/Al (10 cm^3)	373	0.3
iii Mixture of i and ii (10 cm^3 of each)	373	6.8
i 4.4 g Pt/carbon (10 cm^3)	448	1.5
ii 7.0 g Si/Al (10 cm^3)	448	0.9
iii Mixture of i and ii (10 cm^3 of each)	448	6.4

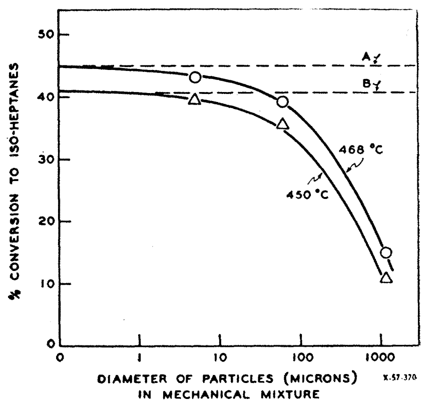

Fig. 1. Isomerization of *n*-heptane over mixtures of particles of silica-alumina and particles of inert-supported platinum. Conversions *A* (468°C) and *B* (450°C) are those obtained over platinum-impregnated silica-alumina.

The ability to feed the olefin isomerization reaction on the silica-alumina (Si/Al) catalyst particles from the low-concentration pool of olefins produced by supported platinum in the same reactor space was tested by observing iso-hexane production in a reactor filled with (i) inert-supported platinum, (ii) particles of silica-alumina, and (iii) a mechanical mixture of inert-supported platinum and particles of silica-alumina, both of 0.84- to 1.4-mm particle size.

Experiments were carried out using a feed rate of 26 cm^3 per hour of *n*-hexane and of hydrogen in a 5/1 molar ratio at atmospheric pressure. Results for the weight-percentage conversion to iso-hexanes in two typical experiments are shown in Table 1. The successful interaction of the two catalyst components by way of gas-phase intermediates to achieve hexane isomerization is apparent from these results.

If the entire reaction rate is thus supported by gas-phase intermediates, the criterion for a critical particle size to obtain maximum conversion will apply, as developed in the previous report (*1*). This was tested in a series of experiments with elevated hydrogen pressure, where side reactions were suppressed; this resulted in substantially clean paraffin isomerization. *n*-Heptane was passed at a space rate of 0.7 g per hour, per gram of catalyst, with hydrogen in 4/1 molar ratio, at 25 atm total pressure.

The conversion to iso-heptanes was determined by mass spectrometer analyses, when, as catalysts, mechanical mixtures of equal weights of Pt-impregnated carriers (approx. 0.3 percent by weight Pt on total mixture) and of silica-alumina (141 m^2/g surface area, 11 percent Al_2O_3) were charged to the reactor. For the 1100-μ size, a loose mixture of the component particles was charged. For the two smaller sizes, the component mixture was compressed into ⅛- by ⅛-in. cylindrical pellets. For compari-